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Trace-Element Characterization of Coal Wastes - Fourth Annual Progress Report

Interagency Energy/Environment R&D Program Report

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TRACE ELEMENT CHARACTERIZATION OF COAL WASTES
FOURTH ANNUAL PROGRESS REPORT

October 1, 1978 - September 30, 1979

by

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ABSTRACT

In the past year we continued our assessment studies of low-sulfur coal wastes from the Appalachian Region. These included mineralogical and trace elemental analyses on these materials and studies of their weathering and leaching behavior. Although the concentrations of the acid-forming minerals (pyrite and marcasite) were very low, leachates were quite acid (pH $\leq$ 3) with concomitant trace element (Al, Mn, Fe, Ni, Cu) concentration elevation. As part of the overall assessment of the degree of environmental concern associated with acidic coal waste drainages, bioassay studies were performed. These revealed that coal wastes and their leachates are toxic to fresh water algae, fathead minnows, and one species of freshwater flea.

Our laboratory experiments to identify control options for the coal wastes and their drainages have been focused on predisposal and codisposal treatments of the waste, with technical and economic evaluations being performed on the most promising options. One of the most promising control methods is pretreatment of the waste with a lime/limestone mixture; this produces a waste with no acid-forming tendencies for times up to several months, during which time it may be possible to dispose of the treated waste in a nonreactive environment. The cost of this option is comparable to that of the commonly used lime neutralization of the acid drainage. Other experiments have investigated, in considerable detail, the economic and environmental advantages and disadvantages of codisposing the wastes with 37 naturally occurring soils and industrial wastes. These methods look promising only under certain conditions, but are in general an order of magnitude less effective than existing controls or the lime/limestone disposal method.

EXECUTIVE SUMMARY

This section summarizes some of the technical highlights, evaluations, and recommendations from the ongoing research program at the Los Alamos Scientific Laboratory (LASL) on the assessment of acid and trace element contamination of aqueous drainages from coals and coal cleaning wastes and from laboratory investigations of environmental controls germane to these problems. Our research has identified the trace elements that are released in concentrations of environmental concern during the leaching and weathering of coal refuse materials from the Illinois Basin and from the Appalachian region. In this report we also include the results of our bioassay evaluations on some of these high-sulfur coal waste leachates. We have established general strategies for the control of these acid and trace element releases and are performing laboratory research to identify the most promising environmental control technologies. These strategies fall into three general categories: refuse treatment prior to disposal, disposal of the refuse in a manner that prevents the release of aqueous contaminants from a refuse dump, and treatment of the contaminated drainages after escape from the refuse pile. The details of these and related research comprise this report of our FY 1979 programmatic accomplishments.

The mineral wastes from coal mining and preparation constitute a potentially major environmental problem. More than 3 billion tons of these refuse materials have accumulated in the U.S., and the current waste production is adding to this at a rate in excess of 100 million tons each year. The number of coal waste dumps is estimated to be between 3000 and 5000; half of these pose some type of health, environmental, or safety problem. Structural weaknesses in coal refuse banks have led to landslides in West Virginia and in Wales, both incurring considerable loss of human life. In addition, there are some 300 burning refuse piles that contribute strongly to the potentially serious air pollution problems of the coal-utilizing areas of the central and eastern U.S. There is also growing awareness and concern about environmental and ecological effects resulting from the trace elements present in acid drainages from coal preparation wastes and surface and underground waterways into which the coal waste leachates drain.

Although it has been known for some time that the drainages from coal wastes may be highly contaminated with trace elements, until just a few years ago little was known about the quantities of undesirable trace elements released into the environment from this source. Since the development of appropriate environmental control technologies for human protection requires quantitative assessment of the extent and severity of the problem, LASL's research, which is supported by the Department of Energy (DOE) and the Environmental Protection Agency (EPA), has included such an assessment program as an integral part of the laboratory investigations of viable environmental controls for the contaminated drainages from coal preparation wastes. Overall, the major objectives of LASL's research program are

- Assessment of the nature and magnitude of trace elements in the effluents from coals and coal preparation wastes,
- Experimental identification of the chemistry of the trace constituents of environmental concern,
- Identification and experimental verification of effective environmental control strategies to control the release of potentially hazardous trace elements, and
- Analysis of the tradeoffs associated with the different control technologies and recommendations for required pollution control or for necessary RD and D programs.

The table on p. 5 is a summary of the trace elements we have identified in leachates from coal preparation wastes and their degree of environmental impact.

During the past year the program included the specific tasks of performing a Level-1 bioassay of coal wastes and coal waste leachates and identifying trace elements of environmental concern in low-sulfur coal preparation wastes from the Appalachian region. The results of the bioassay studies revealed that both the coal wastes and their leachates produce cytotoxic effects and that the leachates are toxic to freshwater algae, fathead minnows, and a freshwater flea (Daphnia). The work on the low-sulfur coal preparation wastes from the Appalachian region has begun to show similarities, in acid-forming character and in leached trace element types, with those of the Illinois Basin.

The research reported here represents a continuation of the studies begun in FY 1976 to establish a firm foundation for subsequent efforts. In the initial period we did the appropriate literature searches, developed laboratory and analytical techniques, collected coals and coal waste samples from several parts of the country, and initiated laboratory studies on the stated objectives. The technical highlights, conclusions, and recommendations resulting from these efforts to date, with detailed emphasis on the accomplishments during the period October 1, 1978 through September 30, 1979, are described briefly in this summary and in detail in the Task Progress Description and in the appendixes.

During the past year the emphasis of our assessment studies centered on low-sulfur (<10%) refuse from a coal preparation plant in the Appalachian region. We performed extensive mineralogical and trace elemental analyses on these materials, and we subjected these mineral wastes to experiments designed to evaluate their weathering and leaching behavior in a coal refuse pile. We then performed trace element analyses on the leachates to quantify the level of pollution caused by the solubilized trace elements. Despite the low concentrations of the acid-forming minerals (pyrite and marcasite), leachates from these waste materials were quite acid with pH values of 3 or lower observed in the dynamic column leachates, and pH values of about 4 in the shaker, batch leachates. These data, when viewed in the context of our past observations that the concentrations of trace elements released by a coal waste are related to the acid-generating tendency of that waste, demonstrate that even low-sulfur wastes have the potential of acting as sources of trace elements in amounts that are of potential environmental concern. These experiments are discussed in detail in the Task Progress section of this report.

Our research in environmental control technology for coal preparation wastes has followed the basic strategy wherein the wastes are

- Treated to make a nonpolluting solid waste,
- Disposed of in a manner to prevent the release of trace elements, and
- Disposed of in a conventional manner, and the drainages treated to remove the trace element contaminants.

Perhaps the most attractive technical solution to the disposal of coal preparation wastes is conversion to a nonpolluting solid. Last year, we reported experimental evidence that calcining converts coal preparation wastes to a nearly neutral, nonpolluting mass. We also reported, however, that the high-sulfur wastes lose 20 - 25% of their weight during calcining and that this is largely due to the release of nearly all (>95%) of the sulfur (as sulfur oxides). Loss of bromine, cadmium, molybdenum, and lead was also observed. Employing technology used in fluidized bed combustion, we have run a number of sulfur-retention experiments in which calcium carbonate has been admixed with ground coal waste before calcining. We found that the sulfur retention is roughly proportional to the added carbonate for all temperatures between 600 and 1000°C, with the maximum sulfur retention (79%) occurring at 800°C. While calcining is clearly an excellent disposal strategy, our economic analysis indicates that this technology is the most expensive option that we have examined.

The second strategem in our control studies assumes that the solid wastes may be disposed of in a manner that prevents the release of trace elements of environmental concern. One method we tried was to slurry the waste with a mixture of lime and limestone. The result was a waste with leachate having a neutral pH and essentially total containment of trace elements. Economically, this treatment was competitive with the most economic control -- effluent lime neutralization; however, the long-term effectiveness of the lime/limestone slurry method is still being investigated in the laboratory and remains a question at this time.

Last year we reported on our initial efforts to locate materials other than lime and limestone that might be codisposed with the coal preparation wastes to produce a nonreleasing system. Our research has broadened to include not only soils with an acid neutralizing ability, but also commonly available natural or industrial materials that appear to have the capability of removing trace elements by a sorbing mechanism. Thus far we have included 37 codisposal agents, among them a variety of calcareous and weathered soils, clays, scrubber sludges, ashes, and specialized materials like peat. In general, these materials were at least an order of magnitude less effective than lime in elevating the leachate pH values and attenuating the trace element concentrations. At this stage in our investigations, we can say that this approach (i.e., use of a sludge to codispose of a coal waste also solves the sludge removal problem) shows considerable promise, but it is clear that the economics are less attractive than the lime/limestone slurry treatment or the effluent alkaline neutralization.

Our third step in the environmental control strategy for high-sulfur coal preparation wastes involves treatment of the leachates. We reported details on a number of water treatment methods last year. Because they treat only a small portion of the potential polluting capacity of the waste, economics and effectiveness are the strong points of these methods. Several, such as reverse osmosis and ion exchange, only concentrate the pollutants and must also include another treatment step.

Alkaline neutralization, which incorporates acidity control, is the best nondestructive control technology that we have found for handling the trace element pollution in coal-preparation wastes. Alkaline neutralization with lime is a state-of-the-art method. Alkaline neutralization is a logical method to use because of its effectiveness, economy, and ease of implementation by nontechnical personnel. Indeed, effluent treatment by alkaline neutralization is the only control technology that has been used to any large extent by the coal industry.

It is clear from our research that similarities and differences exist in the drainages from the coal waste piles in Appalachia and the Illinois Basin. Identification of similarities has the potential of allowing us to generalize environmental controls; recognition of differences will tell us the limits of generic controls. Further research on leachate contamination from more extensive sampling in coal production regions, on generic controls applied to the coal wastes from these regions and their leachates, and on statistical evaluation of these controls and their economic and field-implementation tradeoffs is needed in order that the completed work have a high degree of reliability and not need to be redone for future integrated studies. The impending extensive increase in the use of coal for synthetic fuels, from all the coal regions in the nation, will require assessment and identification of environmental controls far in excess of that which has already been done. A substantial part of our effort will be directed to laboratory research that bears directly on these problem areas.

EVALUATION OF POLLUTING POTENTIAL OF TRACE ELEMENTS IN COAL PREPARATION WASTES[a]

Elements of concern under acid or neutral conditions:
Ni, Mn

Elements of concern under acidic (pH < 4) condtions:
Al, Cd, Fe, Zn

Elements of concern only under highly acidic (pH < 2.5) conditions:
As, Be, Co, Cu, Pb, Se

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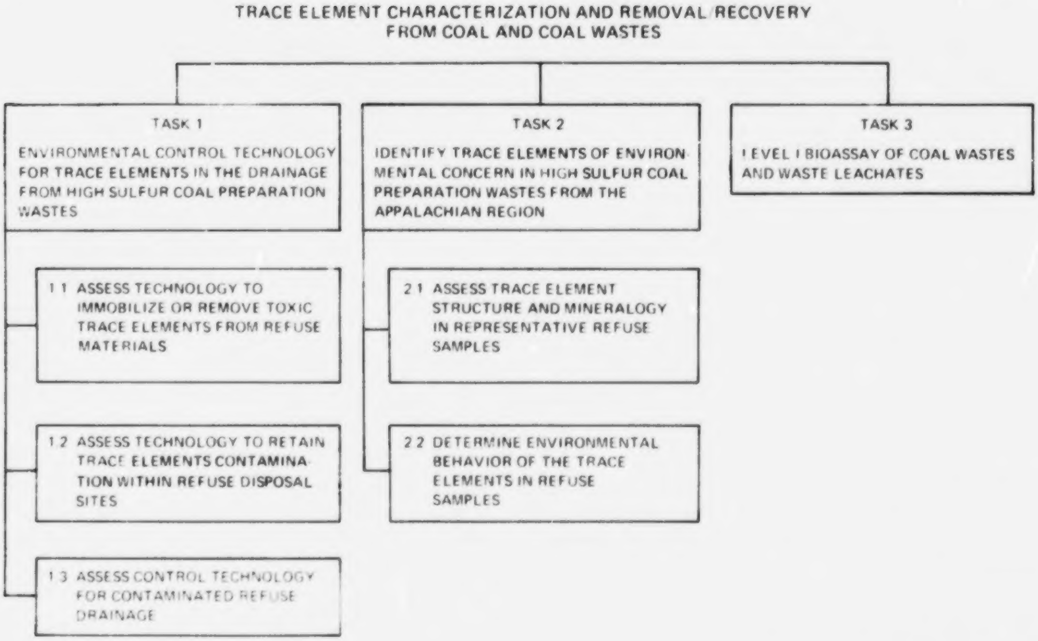
[a] Based on EPA health and ecology MATEs data from column leachates.

CHART OF WORK TASKS FOR FY 1979


TRACE ELEMENT CHARACTERIZATION AND REMOVAL/RECOVERY FROM COAL AND COAL WASTES
TASK 1
ENVIRONMENTAL CONTROL TECHNOLOGY FOR TRACE ELEMENTS IN THE DRAINAGE FROM HIGH SULFUR COAL PREPARATION WASTES
TASK 2
IDENTIFY TRACE ELEMENTS OF ENVIRONMENTAL CONCERN IN HIGH SULFUR COAL PREPARATION WASTES FROM THE APPALACHIAN REGION
TASK 3
LEVEL I BIOASSAY OF COAL WASTES AND WASTE LEACHATES
1.1 ASSESS TECHNOLOGY TO IMMOBILIZE OR REMOVE TOXIC TRACE ELEMENTS FROM REFUSE MATERIALS
1.2 ASSESS TECHNOLOGY TO RETAIN TRACE ELEMENTS CONTAMINATION WITHIN REFUSE DISPOSAL SITES
1.3 ASSESS CONTROL TECHNOLOGY FOR CONTAMINATED REFUSE DRAINAGE
2.1 ASSESS TRACE ELEMENT STRUCTURE AND MINERALOGY IN REPRESENTATIVE REFUSE SAMPLES
2.2 DETERMINE ENVIRONMENTAL BEHAVIOR OF THE TRACE ELEMENTS IN REFUSE SAMPLES

TASK PROGRESS REPORT

The work plan for FY79 called for efforts to be expended in three areas. These areas were designed to 1) determine the nature and magnitude of any problems of environmental concern resulting from trace element release from coal preparation wastes (Task III); 2) evaluate the extent and cause of problematic areas (Task II); and 3) perform the research necessary to develop suitable environmental controls (Task I). In the past 3 yr of the project, Tasks I and II have received the major fraction of the effort. Task III was included this year to substantiate, with biological evidence, the concerns that had already been identified based on chemical evidence. We have also extended our study to include a wider range of coal types. Because our research shows that the polluting potential of coal preparation wastes is of environmental concern, our effort has continued to be concentrated into finding viable technical and economical control methods. Following the described waste disposal strategies, we have identified and evaluated a variety of control technologies.

I. TASK I: ENVIRONMENTAL CONTROL TECHNOLOGY FOR TRACE ELEMENTS IN THE DRAINAGE FROM (HIGH-SULFUR) COAL PREPARATION WASTES

One of the primary reasons for studying the releases of trace elements from high-sulfur coal preparation wastes is to provide necessary information about the nature and magnitude of this form of pollution to plan and develop environmental control strategies for coal refuse dumps and disposal areas. The research done in the early years of the program has provided us with a broad base of information and understanding that we have used in our environmental control activities. This task describes the work done in this area. Also included in our discussion are economic and physical aspects of the various controls investigated, and we have kept in mind potential impacts on solid waste disposal of the Resource Conservation and Recovery Act (RCRA).

A. Waste Disposal

The ultimate waste disposal scheme is one that blends the waste into the environment with no detrimental effects. Because burial restricts wind and air access, water flow, and temperature fluctuations, it also restricts pollutant movement and is a possibility that should be considered. The major problem with the burial of coal refuse is that, in many parts of the country (especially where most of the acid-generating coal is mined), it is difficult to identify underground burial sites where ground or surface water will not eventually intrude into the area. This intruding water can dissolve latent pollutants, allowing them to get into general water systems. The possibility that this influxing water can be acidic, as the result of acid mine drainage or acid rains, may compound the problem when disposing of coal wastes in the coal mining terrains of the East and Midwest.

Burial sites for coal refuse are often located in hollows or valleys, where the wastes are compacted into layers, covered with topsoil and revegetated. Increasingly, these waste materials are also being deposited into depleted strip mines, and the possibility of disposal in underground mines is being explored. Schematics of these methods are presented in Fig. 1. It appears that both near-surface and strip or deep mine burial of coal wastes will require measures to prevent or minimize pollution of ground water. There are certain natural mechanisms that may help to keep such contamination within acceptable limits, however. These include sorption processes in rocks and soils, precipitation, coprecipitation, dilution and dispersion of contaminants by the natural water system, and biological activity. The effectiveness and magnitude of treatment offered by these or other natural mechanisms depend on the geological and hydrological conditions at a specific site. In many cases the degree of buffering, attenuation, and dilution by aquifers is not

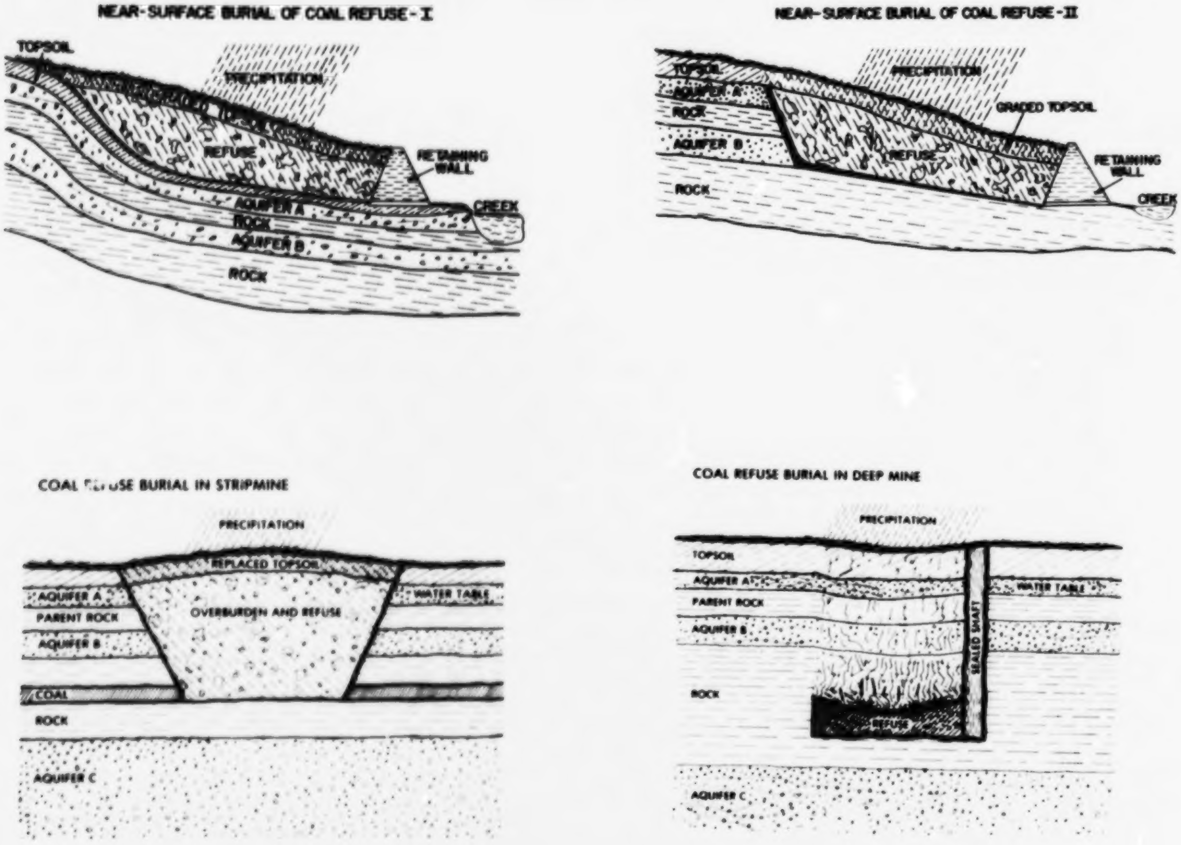

NEAR-SURFACE BURIAL OF COAL REFUSE - I
TOPSOIL
PRECIPITATION
GRADED TOPSOIL
REFUSE
RETAINING WALL
CREEK
AQUIFER A
ROCK
AQUIFER B
ROCK
NEAR-SURFACE BURIAL OF COAL REFUSE - II
TOPSOIL
AQUIFER A
ROCK
AQUIFER B
PRECIPITATION
GRADED TOPSOIL
REFUSE
RETAINING WALL
ROCK
CREEK
COAL REFUSE BURIAL IN STRIPMINE
PRECIPITATION
REPLACED TOPSOIL
AQUIFER A
WATER TABLE
PARENT ROCK
OVERBURDEN AND REFUSE
AQUIFER B
COAL
ROCK
AQUIFER C
COAL REFUSE BURIAL IN DEEP MINE
PRECIPITATION
TOPSOIL
AQUIFER A
WATER TABLE
PARENT ROCK
AQUIFER B
SEALED SHAFT
ROCK
REFUSE
AQUIFER C

Fig. 1.
Schematics for several coal waste, burial scenarios.

known. In these cases, it would be difficult to predict reliably how much natural attenuation of trace elements or other contaminants would occur. It seems advisable, however, to let nature help. Wastes could be placed under temporarily nonpolluting conditions that would allow time for natural assimilation of the waste into the environment.

The high-sulfur coal preparation wastes have significant trace-element polluting potential, resulting from pyrite oxidation. We have found damp, oxidizing conditions to be the worst of all. Disposed of in an untreated state, the waste must be isolated and any effluent must be treated. Such containment is sometimes feasible over the short term but impractical to guarantee over the long term. The widespread pollution from acid mine drainage (AMD) is an excellent example of the difficulties that can arise. Attempts to control AMD have met with limited success, and long-term solutions seem lacking or prohibitively expensive. Placing coal refuse under similar conditions in deep mines could create new problems or aggravate an old one. Polluted drainage could continue for a long time (see Appendix O for time calculation). In addition to air and water intrusions, near-surface and strip-mine sites are subject to erosion by wind and floods. Sites designed to completely contain or channel the pollutants may also be subject to earthquakes, tremors, roots of trees and other plants, and burrowing animals. All these work to undermine burial scenarios based entirely on containment and subsequent treatment by conventional means.

Ideal waste disposal sites would contain the pollutants completely, release them at environmentally acceptable rates, or deliver them for treatment at some collectible point. This is the crux of our waste control philosophy: address the waste first, the disposal site next, and the polluted discharges last. This approach is depicted in Table I. While methods designed to treat the waste and make it innocuous are most effective, other factors (e.g., economic positions) may favor other control measures. For these reasons, our research efforts have mainly been directed at the technical feasibility of various control methods. Numerous questions may arise for the various options considered. Some of the more recurrent questions are listed in Table II.

TABLE I

WASTE CONTROL APPROACHES

Approach	Disposal Method	Leachate	Comment
Waste	Nonpolluting	Clean	Minimal environmental impact
Disposal Method	√ Nonpolluting	Clean	Compliance red tape
Leachate	Polluting	√ Polluted	Perpetual, elusive pollution

TABLE II

SOME ISSUES TO BE CONSIDERED WHEN ADDRESSING CONTROL TECHNOLOGIES FOR TRACE ELEMENTS IN COAL REFUSE DRAINAGE

- Effectiveness for treating or preventing the type and quantity of trace element contamination expected for refuse dump drainage
- Effectiveness of method for treating widely varying volumes of contaminated drainage
- Mechanism of process; what makes it work?
- Specific or general trace element removal
- Restrictions or shortcomings of method
- Time required to set up technique
- Special skills or training necessary to operate method
- Necessity for frequent or extensive maintenance or replacement
- Present state of development
- Current use; where and for what?
- Does expertise with the method now exist? Where and with whom?
- Expendable materials requirements; availability and transportation requirements
- Probable reliability
- Feasibility for use in coal industry
- Long and short term use implications; economic, technical, and environmental
- Potential for mineral or metal recovery
- Necessity of additional feasibility or assessment studies
- Capital equipment needs and costs
- Operating equipment needs and costs
- Comparative or absolute economics

B. Altering the Waste

One good technical solution to the disposal of a hazardous, polluting waste is the conversion of this waste to a nonpolluting one.

Last year, we reported experimental evidence that calcining converts high-sulfur coal preparation wastes to nearly neutral and nonpolluting systems. This is achieved with only moderate change, some sintering, in the outward appearance of the wastes (see Fig. 2). We also reported, however, that the waste loses 20 - 25% of its weight during calcining and that this is largely due to the release of nearly all (>95%) of the sulfur (as sulfur oxides). Bromine, cadmium, molybdenum, and lead were also observed to be lost. Treating the effluent gases from calcining would be akin to flue gas desulfurization (FGD) at a power plant. In the following paragraphs, we describe experiments to retain the sulfur in the calcined waste and present a discussion of the leaching behavior of such a calcined waste.

Employing technology used in fluidized bed combustion, we have run a number of experiments in which calcium carbonate has been admixed with ground coal waste before calcining (see Appendix A). Because solid/solid and solid/gas reactions are occurring, the method can give varying degrees of sulfur retention, depending on the concentrations and physical nature of the components and the temperature of the calcining. Sulfur retention is roughly proportional to the added carbonate (as measured by the Ca/S ratio)† for all temperatures between 600 and 1000°C (see Fig. 3). The exact proportionality, however, is temperature related with the maximum retention corresponding to 800°C (see Fig. 4).* This

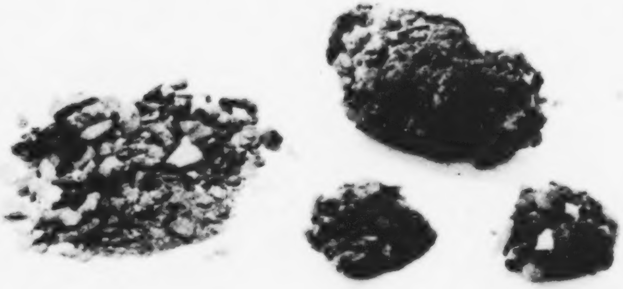


Fig. 2.
Particle sintering of calcined coal preparation waste.

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†At a Ca/S = 1 ratio, 12 grams of calcium carbonate are added to 30 grams of waste.

*Dry mixing of powdered ferric oxide and granular sodium chloride additive did not improve sulfur retention.

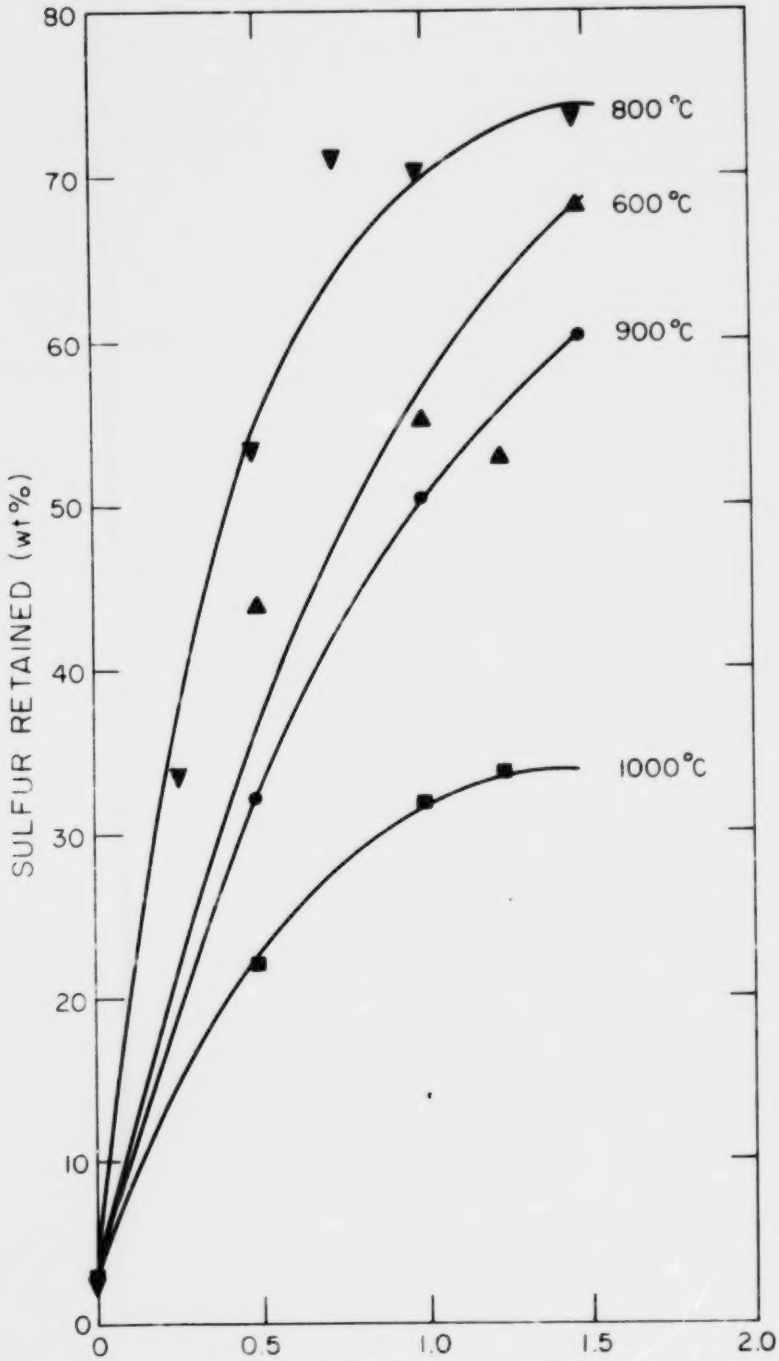

Fig. 3.
Sulfur retention as a function of calcination temperature and Ca/S molar ratio.

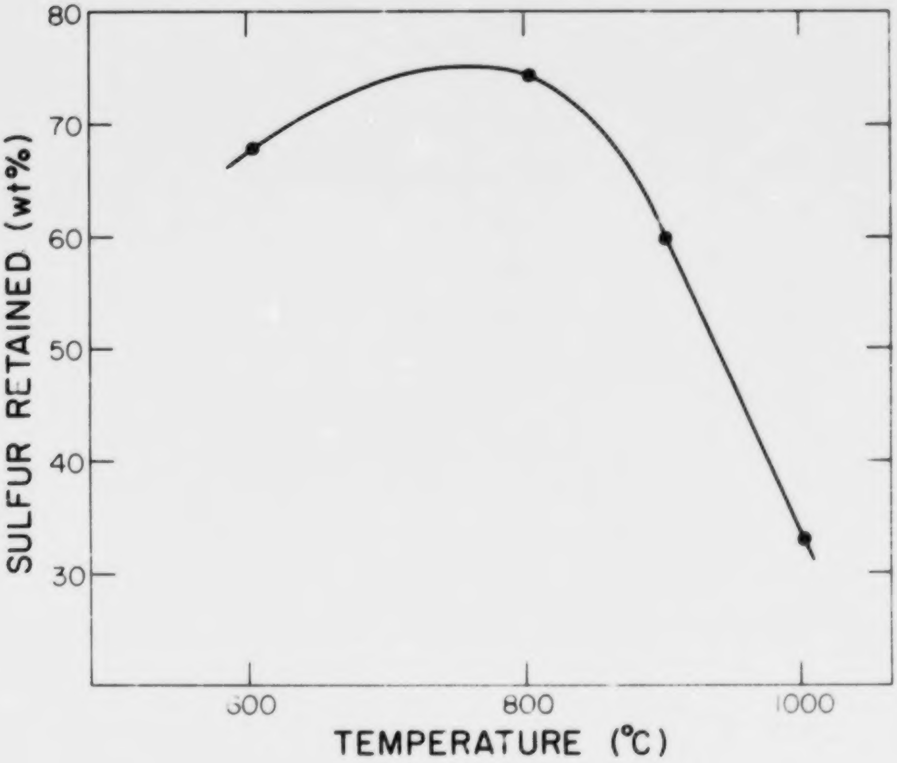

Fig. 4.
Sulfur retention as a function of temperature at Ca/S = 1.5.

temperature corresponds to the disappearance of the XRD lines that identify the clay components (third annual report, LA-7831-PR, p. 9). Above this temperature, the sulfur-containing species begin to release sulfur dioxide and revert to the more stable oxide. At 1100°C, practically no sulfur (<0.1%) is retained.

Smaller particles of waste and calcium carbonate combine to give more contact area and, hence, higher sulfur retention than do larger particles containing the same amounts of the sulfur and carbonate reactants (see Fig. 5).† Increasing the contact area by reducing the size of either component improves the S retention (compare the half-shaded square with the open squares of Fig. 5). More dramatic improvement results when the components are slurry mixed (compare the solid and half-shaded squares of Fig. 5).

Based on these findings, large quantities of coal wastes would have to be handled in the treatment process and also be ground to fine particle sizes if most of the sulfur were to be retained in the waste mass

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†Volumes occupied by 1 gram of material are 0.8 cc for -10+32 mesh waste and limestone, 1.2 cc for -20 mesh waste, and 3.0 cc for AR calcium carbonate.

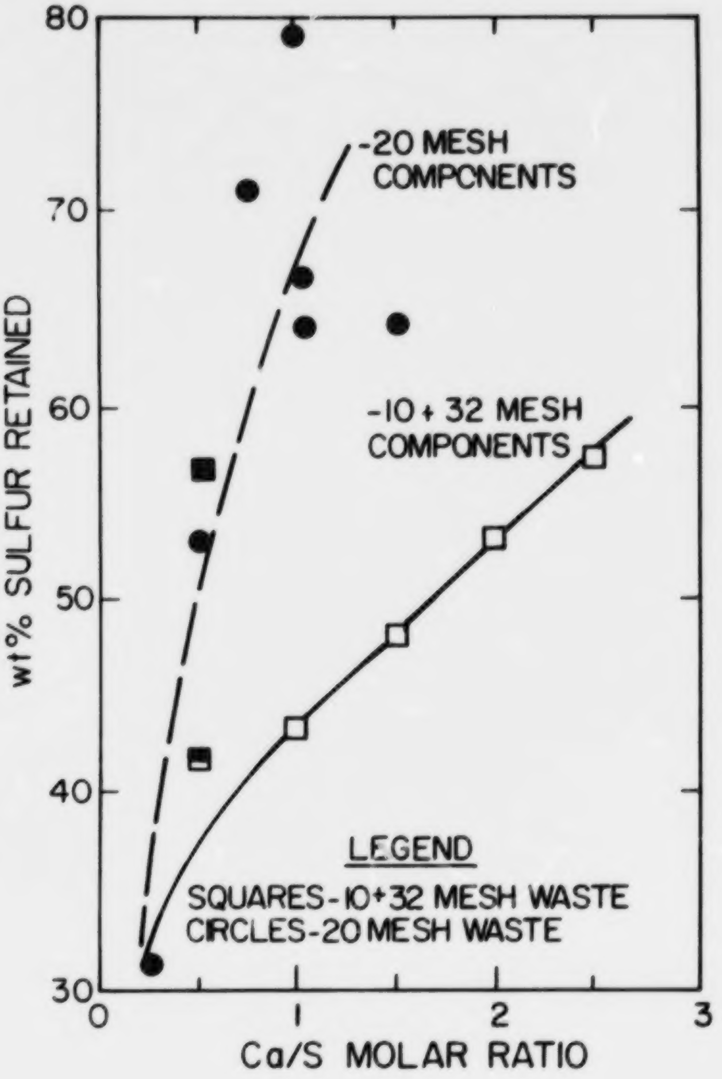

Fig. 5.
Effect of physical proximity on the retention of sulfur during coal waste calcining with dry-mixed carbonate. (-115 mesh $CaCO_3$ used in shaded square. Slurry mixing for solid square.)

during calcining. Under the best experimental conditions used, 20% of the sulfur is off gassed. If calcining is to be employed, the best procedure seems to be to concentrate the sulfur-control effort entirely in the off-gas area by employing FGD technology.

Calcined coal preparation wastes form nearly neutral leachates which increase slightly in alkalinity as the calcining temperature increases (see Fig. 6). Likewise, the release of trace elements is dramatically

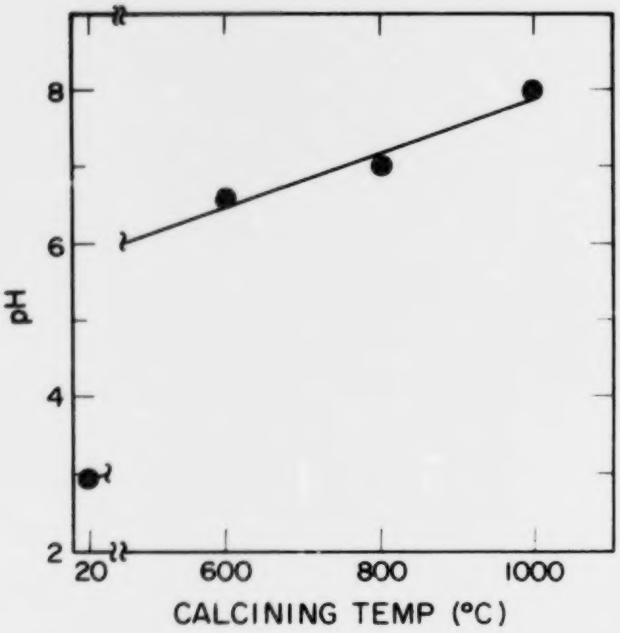

Fig. 6.
Leachate pH for coal waste calcined at various temperatures.

changed. Except for calcium, all the elements studied have lower concentrations as the result of calcining (see Table III and Appendix A.) This decrease is somewhat temperature related with manganese requiring higher temperatures than other elements to be reduced. At 1000°C, values for all elements, except that for calcium, are below the EPA ecology MATE levels (see Table III and the discussion on bioassay under Task III). No particle size effect occurs over the narrow range of -20 to -10+32 mesh. If limestone is added to reduce gaseous sulfur oxide emissions, the excess carbonate forms lime, which gives a very alkaline (pH 12) leachate (see Ca/S = 1.0 in Table III). Retained sulfur in the calcined waste does not diminish the effectiveness of the calcining treatment in decreasing trace element releases from coal preparation wastes to aqueous media.

The sensitivity that we have observed in the laboratory of the calcined waste to acid leaching suggests that the reduction in leachability by water might be pH controlled. Indeed, where the pH of the uncalcined control was changed from 2.9 to 8.1, the elemental levels in the leachate were not significantly different from those found when a similar pH is formed by a calcined waste (see data corresponding to pH 8.0 and pH 8.1 in Table III). The iron values differ, because substantial amounts of ferrous ion are present in the uncalcined leachate before neutralization. The main function of calcining at these temperatures, therefore, appears to be one of rendering the waste incapable of acid production by eliminating the oxygen-unstable sulfur species and thus allowing natural pH-controlled leaching to occur.

TABLE III

EFFECTS OF CALCINING CONDITIONS ON AQUEOUS TRACE ELEMENT RELEASES FROM CALCINED COAL WASTES[a]

Temp (°C)[b]	Ca/S[c]	Leachate[d]	pH	TDS(%)	Al	Ca	Cd	F	Fe	Mn	Na	Zn
Control	0	Water	2.9	0.63	100	550	0.068	14	600	5.8	76	2.8
600	0	Water	6.6	0.38	<0.8	610	0.005	0.5	<0.05	4.2	73	0.35
800	0	Water	6.9	0.33	0.38	560	0.0008	-	0.5	3.2	-	0.43
"	1.0	"	12.4	0.34	0.6	900	0.0006	-	0.05	0.03	-	0.11
1000	0	Water	8.0	0.17	0.4	400	0.0002	1	<0.03	0.03	12	0.05
"	0	0.4M H_2SO_4	2.9	0.5	88	580	<0.0008	40	25	1.2	30	3.8
pH Controlled Leachate[e]	-	Water + Lime[e]	8.1	-	<0.1	500	<0.009	10	2.2[f]	0.3	-	<0.02
Ecological MATE Values	-	-	-	-	1	16	0.001	-	0.25	0.1	-	0.1

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[a] Element values in mg/ℓ.
[b] Calcined in muffle furnace for 2h.
[c] Calcium to sulfur molar ratio for added calcium carbonate.
[d] 48h leach, 4 mℓ leachate per gram waste, open to air, magnetically stirred.
[e] From Table F-I on alkaline neutralization of coal waste leachates.
[f] Ferrous cation accounts for nearly all the iron present.

Forming cement blocks from the waste is a method of altering the waste which does not require the expensive on-site furnaces, etc., required by the calcining process. To evaluate the potential of this technique, we have prepared small (2.5-cm-high by 3-cm-diam) cylinders using fine (-20 mesh) coal waste as the aggregate (see Appendix B). The mixes for these cylinders were prepared as variations on the ASTM formula for mortars, i.e., one part portland cement, one-half part hydrated lime, and three parts fine aggregate (see Table IV). Even though the cylinders were small, they began to spall as the aggregate level was increased above the norm. At high aggregate loading (1 cement:1/2 lime:12 aggregate) and lower loadings without lime (1:0:6), the cylinders rapidly disintegrated when placed in water. For structural integrity to be maintained, the coal-waste concrete blocks will need to be richer in cement and lime.

Leachates in contact with the coal-waste cement cylinders were initially quite alkaline (see Table IV). The pH values dropped as fresh water was brought into contact with the solid. After five water changes, the pH values were down to 9 and leveling off. Trace element levels at this point were well below levels of concern (see Appendix B). As with the calcining method, the major effect here is probably pH control. One of the leached specimens (1:1/2:6) spalled but still gave acceptable leaching behavior; higher loading of waste materials will be possible if lower structural requirements are acceptable.

Waste alterations could provide an excellent way to dispose of coal preparation wastes. Removal of the acid-generating components via calcining appears to be an excellent predisposal treatment for coal preparation wastes in order to release potentially hazardous levels of trace elements. Our analysis reveals, however, that calcining is an expensive option.

TABLE IV

STRUCTURAL STABILITY AND LEACHATE pH FOR MORTARS FROM FINE COAL PREPARATION WASTE

		Leachate pH	
Mix[a]	Structural Stability	Initial	5th Rain[c]
1:1/2:3	Sound: sand control[b]	11.5	9.0
1:1/2:3	Like sand control	11.5	9.0
1:1/2:6	Some cracking on drying	11.5	8.9
1:0:6	Disintegrated within 1 minute in water	-	-
1:1/2:12	Disintegrated within 1 hour in water	-	-

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[a] Volume parts of portland cement:hydrated lime:-20 mesh waste.

[b] Sand used instead of waste.

[c] Each rain of 250 mℓ was in contact with cylinder for several days to weeks.

C. Moderating the Disposal Site with Abators

The second option in our control strategy uses the approach that a hazardous, polluting waste can be placed in a disposal site in such a way that it will release pollutants at an acceptable level. Coal production for energy produces several large-volume waste problems. Large acreages of overburden are disturbed; acidic coal preparation wastes are produced; and fly ash, bottom ash, and sludges from flue gas scrubbers are generated. Each poses a disposal problem of its own. Conceivably, two or more of these problems can be handled together to create a single waste with more desirable characteristics. (This may be practical where mine mouth plants are operated.) Our objective here has been to evaluate ways that coal preparation waste can be codisposed to produce acceptable leachates and ways other coal production and utilization wastes can be used in achieving a symbiotic codisposal scheme.

In our third annual report (LA-7831-PR), we related our partially successful efforts to dry-mix coarse (-3/8-in.) limestone with acidic coal preparation waste and pass the leachate through crushed (0.84-mm) limestone. By using hydrated lime slurries, however, acceptable leachate levels of trace elements could be obtained, but the pH levels were difficult to control and often were very high. We have continued this series of experiments to determine whether fine-particle limestone slurries could give acceptable leachates with regard to both trace element and acidity levels.

Calcium carbonate was added to acidic coal-preparation waste in four ways. A short tabulation is given in Table V. (Full descriptions and results appear in Appendix C.) In CTWT-11-6, the calcium carbonate was produced by converting most of the unneutralized lime to $CaCO_3$ with carbon dioxide. In CTWT-11-8, some of the acid present was neutralized by

TABLE V

CALCIUM CARBONATE TREATMENTS OF COAL WASTE[a]

Sample No.	Neutralizing Agent			Type of Mixing	Initial pH
	Additive	Size	(%)		
CTWT-11-6	$Ca(OH)_2 + CO_2$	-100 mesh	5.0	Slurry	7.4
CTWT-11-7	$CaCO_3$	-100 mesh	6.7	Slurry	6.9
CTWT-11-8	$Ca(OH)_2$ + $CaCO_3$	-100 mesh -100 mesh	1.5 4.0	Slurry	6.2
CTWT-11-9	Limestone	-20 mesh	6.0	Slurry	6.4

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[a] -3/8 inch Plant B average coal waste.

first adding lime, then adding the calcium carbonate. The first three treatments have comparable acid neutralizing equivalences, while CTWT-11-9 has less.

Two of the four slurry-effected calcium carbonate treatments produced coal wastes which gave acceptable leachates. The other two were close (see Fig. 7). Even after exposing to air to induce oxidation, the fine-particle calcium carbonate treatment (CTWT-11-7) continued to produce leachates with pH values of 6 to 9. The others were less effective but returned to acceptability with a water flow. The main solids load of the leachates was calcium sulfate. Trace element concentrations (except for fluorine) dropped as increasing amounts of leachate passed through the treated waste. (See Fig. 7 for Fe and Mn. Other elements are

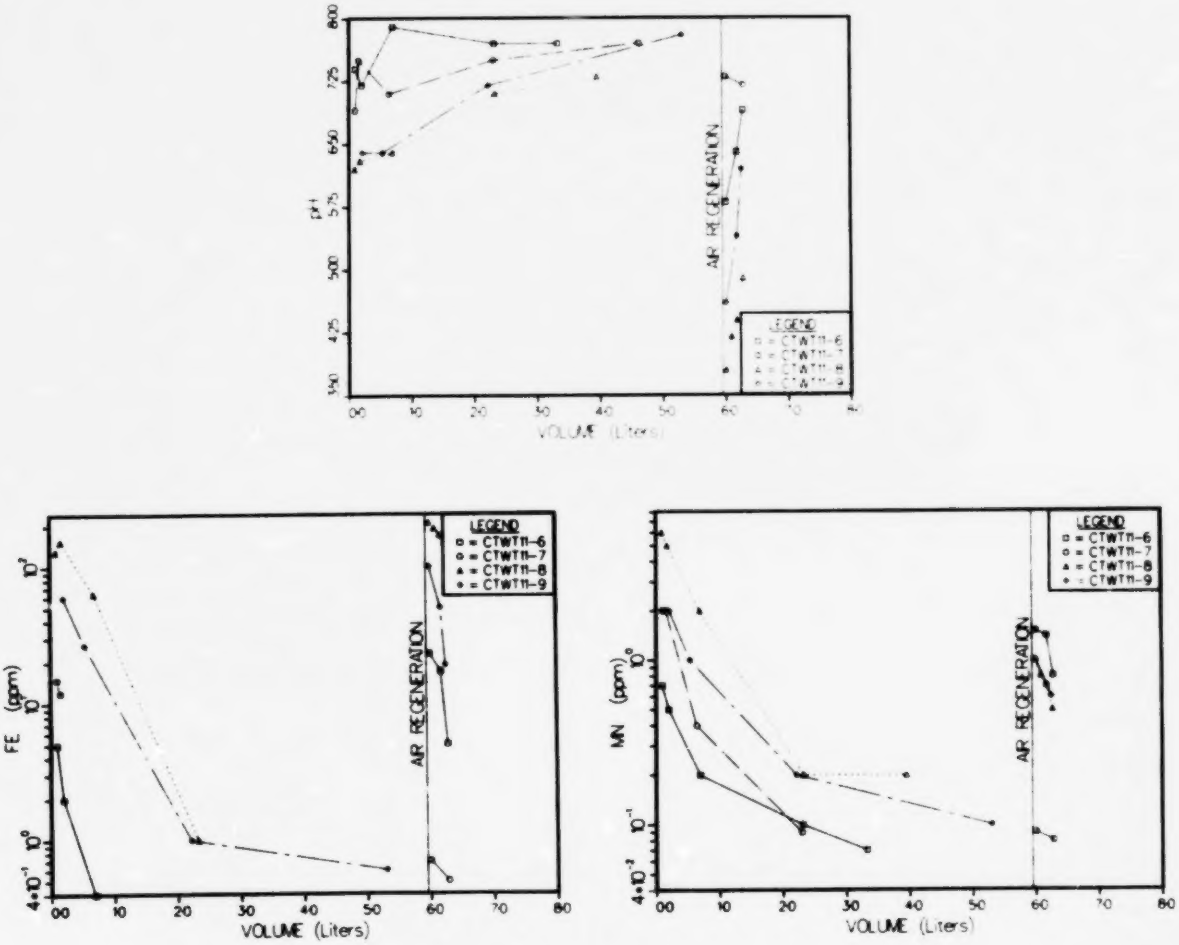

Fig. 7.
The pH, iron, and manganese levels in leachates from coal wastes slurry treated with alkaline agents.

reported in Appendix C.) Forced oxidation elevated the trace element level. Ecological discharge severity factors* for the initial leachates from each treatment show acceptable levels for all trace elements except iron and nickel, and these were acceptable when the treatment raised the pH level to 7 (see Table VI).

Adding a neutralizing agent to coal-preparation waste materials during disposal can be effective in moderating the trace element discharges. Combined with soil attenuation (see below and the section on "Pollutant Attenuation and Movement through Soils"), this technique could provide an orderly assimilation of coal waste into the environment without dump liners, addition of sorbents, neutralizing soils, etc. Slurrying of fine particulates with neutralizing agents is needed. Excess agent needs to be added to handle further oxidation encountered during delays in burying the waste. A short "soak" or aeration time (several days at pH > 7) before burying would allow oxidation of ferrous ions to ferric ions and eliminate the last bit of soluble iron. High pH values are not necessary, but a little excess lime would shorten this "soak" time. Indeed, these experiments have been quite encouraging.

TABLE VI

DISCHARGE SEVERITY FOR CALCIUM CARBONATE TREATMENT OF COAL WASTES[a]

	Treatment Number			
Parameter	**CTWT-11-8**	**CTWT-11-9**	**CTWT-11-7**	**CTWT-11-6**
pH	6.2	6.4	6.9	7.4
Al	<0.005	<0.005	<0.005	<0.005
Ca	0.4	0.4	0.4	0.6
Cd	0.06	0.02	0.03	0.02
Co	0.06	0.02	0.001	0.005
Cr	<0.00002	<0.00004	<0.00002	<0.00002
Cu	<0.02	<0.02	<0.02	0.02
F	0.0004	0.0004	0.0005	0.0008
Fe	5.2	2.4	0.6	0.2
K	0.003	0.002	0.004	0.003
Mn	0.6	0.2	0.2	0.007
Na	0.0001	0.00008	0.0002	0.00009
Ni	2.4	0.9	0.8	0.3
Zn	0.04	0.01	0.006	0.007

[a] Discharge severity = Concentration in ppm/100/MATE in ppm.

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*These include a 100-fold "environmental" dilution of the leachate.

In our third annual report (LA-7831-PR), we reported initial efforts to locate materials other than lime and limestone that might be codisposed with coal preparation waste to produce an acceptable waste system. We have now broadened our search to a wider sampling of possible sorbents. Special precautions have also been taken to evaluate oxygen-sensitive ferrous ions. Up to six successive batch encounters between a leachate and a new portion of sorbent have been run to quantify the attenuating power of the materials. These efforts have much broader application than just codisposal, however. The data generated also reflect migratory behavior through these materials (see the section on "Pollutant Attenuation and Movement through Soils") and thus indicate the suitability of an area as a coal-waste disposal site.

A major requirement of a sorbent for coal-waste codisposal is its ability to handle the acid generated. Natural and process waste sorbents show a wide range of effectiveness. Most of the 22 materials listed in Table VII have acid-attenuating capability. Under test conditions

TABLE VII

SORBENTS TESTED FOR THEIR ABILITY TO ATTENUATE COAL WASTE ACIDITY

Sample No.*	Material
1	Alluvial Soil
2	Organic Soil
3	Glacial Till
4	KY S-12 Overburden
5	KY S-11 Overburden
6	Glacial Till
7	Loess Soil
8	Glacial Till
16	Loess Soil
19	Loess Soil
20	Montmorillonite
21	Kaolinite
25	Peat
26	Western Coal
27	AR Calcium Carbonate
28	Quarry Limestone
29	Limestone Scrubber Sludge
30	Economizer Ash
31	Precipitator Ash
33	FGD Scrubber Sludge
34	ESP Ash
-	Hydrated Lime

*These numbers correspond to those used in other tables and graphs in this section.

designed to emphasize soil attenuation of acid and trace metals, many sorbents are within a factor of 2 of being as effective as powdered calcium carbonate. All other things being equal, it is reasonable to assume the carbonate content of the soils would be the major factor in their ability to neutralize the acidity of coal waste leachates. However, Fig. 8 suggests that other mechanisms are operational as only a fraction of the stoichiometric amount of carbonate is utilized, and this fraction varies considerably from one soil to another. Soils containing little carbonate perform almost as well as calcium carbonate does. Almost none of the soils do as well as they could if they used all of their carbonate.

Carbonate utilization by the soils appears in part to be related to particle size at all carbonate levels. Identifying the sorbents with similar-mass median particle sizes, we find two groups that explain much of the vertical scatter (see Fig. 9). Thus, at any given percentage of carbonate, about twice as much -100 mesh soil is required to neutralize the same quantity of coal waste leachate as that neutralized by a -200 mesh soil. We have noted a similar particle size effect in previous column attenuation experiments with limestone. This effect apparently results from deactivating the calcium carbonate by coating the particle

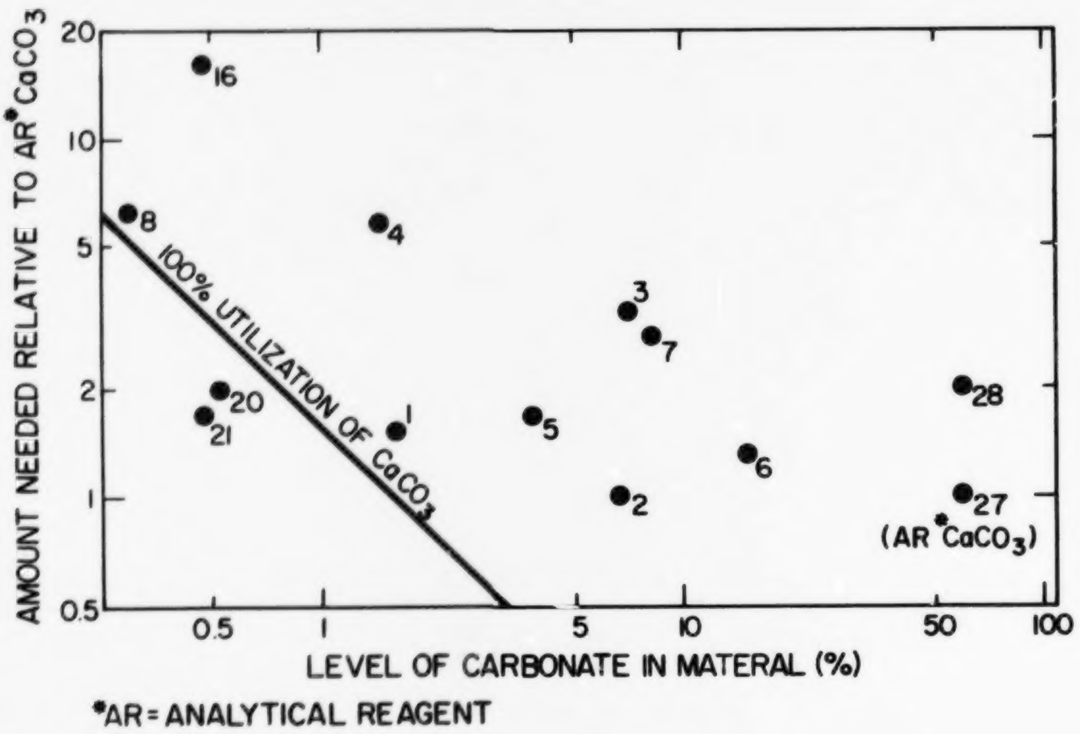

Fig. 8.
Relative amount of natural sorbent needed to attenuate coal waste acidity as a function of the carbonate level in the sorbent.

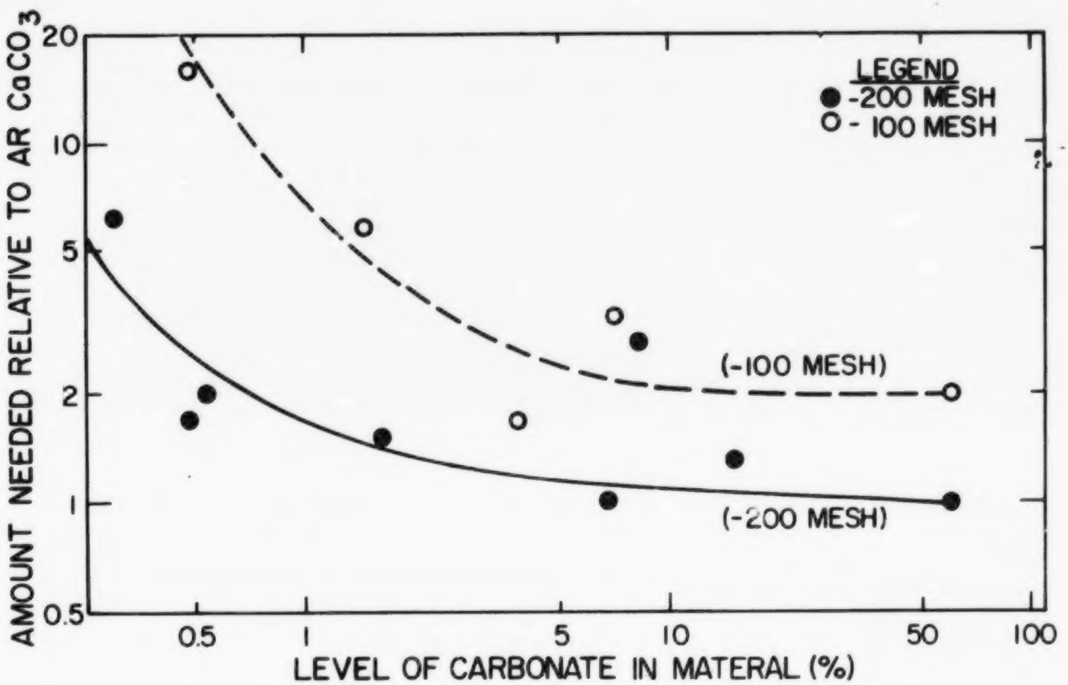

Fig. 9.
Relative amount of natural sorbent needed to attenuate coal waste acidity as functions of the carbonate level and particle size of the sorbent.

surfaces with layers of $Fe(OH)_3$ and/or $CaSO_4$. Such an explanation is consistent with the approximate two-fold decrease in carbonate required to neutralize coal waste leachate acidity in going from -100 mesh (149-μm) to -200 mesh (74-μm) soil particle size. Spherical particles of 74-μm diameter have twice as much surface area per unit mass as 149-μm spherical particles. We expect that the neutralizing efficiency of calcareous materials will continue to decrease as the particle size increases. Thus it is important to classify potential sorbents as to their effectiveness at the same particle size or under the actual physical conditions to be used in the field.

The poor neutralizing power at high carbonate levels is a consequence of using an experiment designed to evaluate trace-element attenuation at a high solids-to-leachate ratio also as an experiment to determine acid neutralizing stoichiometry. Calcium carbonate, being a weak base, forms a buffer at a pH value around 6 in the presence of a strong acid, such as H_2SO_4. As long as the acid added is less than the stoichiometric amount of calcium carbonate, addition of more carbonate will not greatly alter this pH. However, when this leachate is equilibrated with new soil, a small change in pH to 7 is effected, and the end point is achieved. This is quite different from lime, a strong base, which is highly soluble and gives high pH values when over-neutralizing an acid.

This buffering capacity of calcium carbonate is apparent from our experimental data plotted in Fig. 10, where a sulfuric acid solution with total acidity comparable to the coal waste leachate, but without its chemical constituents, is agitated with soil at a 2:1 liquid-to-soil ratio. About 1.7% carbonate is needed in the soil to neutralize the 0.14M H_2SO_4. This amount of carbonate is stoichiometrically equivalent to the amount of sulfuric acid present. Adding more than the stoichiometric amount of soil or calcium carbonate material in the first equilibration will result in unused or wasted base and will cause the material to be underestimated in its neutralizing ability. For analytical reagent (AR) $CaCO_3$ this amounts to a 36-fold lower rating. The effect of equilibrating nearly equal quantities of materials with coal waste leachate is to level the

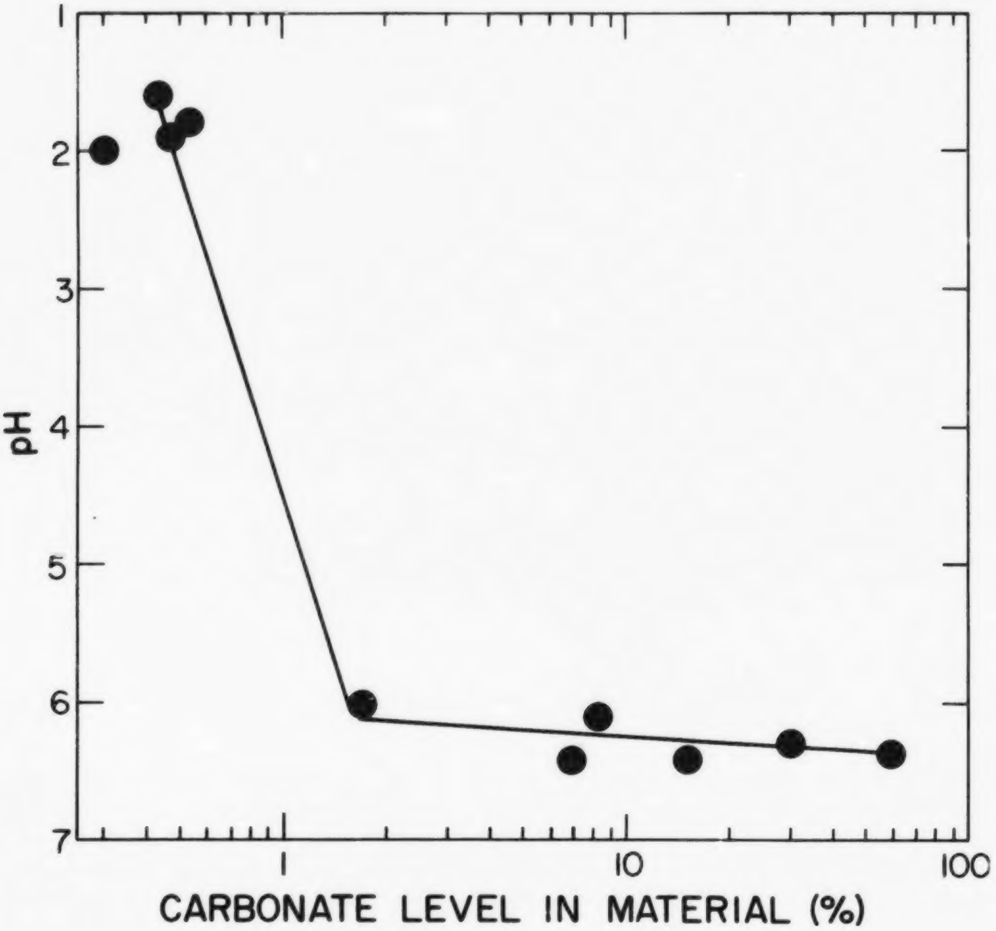

Fig. 10.
The pH of 0.14M sulfuric acid solutions treated with natural sorbents having different carbonate contents. (Liquid:solid ratio is 2:1.)

calcareous materials with more than the stoichiometric amount of calcium carbonate into a poorly differentiated group.*

If we wish to compare the capability of the various sorbents to attenuate contaminant levels in coal waste leachates, we must adjust our results for carbonate content above the stoichiometric amount required to neutralize a given quantity of acidity and for particle size differences. Normalizing the coal waste leachate sorbent data for these variables, we have generated a semiquantitative rating of the ability of the tested sorbents to control acidity (see Table VIII). In general, most sorbents

TABLE VIII

SORBENTS RATED FOR THEIR ABILITY TO ATTENUATE COAL WASTE ACIDITY

Material	Sample No.	Weight per Equivalent (tons lime)	
		Adjusted[a]	As-measured[b]
Hydrated Lime		1	1
AR $CaCO_3$.	28	2	50
Quarry Limestone	27	2	100
Limestone SS	29	4	80
Glacial Till	6	6	60
Organic Soil	2	10	50
Loess Soil	7	14	150
Glacial Till	3	18	150
FGD SS	33	22	350
KY S-11 Overburden	5	30	80
Alluvial Soil	1	50	80
EC Ash	30	60	60
KY S-12 Overburden	4	60	300
Precipitator Ash	31	80	80
Kaolinite	21	80	80
Montmorillonite	20	100	100
Loess Soil	16	150	800
ESP Ash	34	250	250
Glacial Till	8	300	300
Western Coal	26	900	900
Loess Soil	19	>600	>600
Peat	25	∞	∞

[a] Adjusted for particle size and "underestimation"; see text.

[b] From Appendixes D, E, and F.

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*Researchers who want to devise a single-equilibration, batch experiment to evaluate soils, especially for attenuating power and transport potential, should note that quantities of pollutants in relation to available soil sites may be more important than the ratio of the liquid to the solid. Column schemes may be more appropriate than batch ones. For acid neutralizing ability, a titration method seems the best characterization tool. In any case, the importance of various parameters, such as physical size, needs to be understood to properly evaluate and apply laboratory results.

are at least a factor of 10 poorer than lime. Since many of the natural sorbents, such as limestone and overburden materials, are unlikely to be crushed below -3/4-in. in field codisposal use, their ratings should probably be at least another order of magnitude poorer. Scrubber sludges and fly ashes, being process wastes and crushed finely, would not have a similar reduction due to size.

The ability to attenuate trace elements released by the coal preparation waste is another important requirement of a sorbent. Qualitative evaluations of the abilities of numerous sorbents to control 13 elements of interest released by coal wastes are given in Tables IX and X. (In most cases these evaluations are based on three to five equilibrations of the leachate with fresh sorbent. See Appendixes D and E for details and elemental levels.) Sorbent attenuation of trace elements is roughly related to the sorbent's ability to attenuate acidity. Thus, those sorbents unable to handle the acidity are likewise unable to handle the trace elements. Notable exceptions to this rule are the natural (humic) species, peat, and subbituminous (NM) coal. In our experiments, sorbents with 1/300th the neutralizing strength of hydrated lime were able to handle the acidity. More importantly, all soils showed some attenuation of nearly all the elements studied.

Differences among the tested sorbents as to their abilities to control trace elements when the acidity is controlled (pH > 7) are not easily recognized. More noticeable are the differing responses of the trace elements, regardless of sorbent. Four groupings are needed to describe attenuating behavior from excellent to poor (see Table XI). Iron (ferric state) and aluminum are very pH-sensitive and well attenuated. Iron (ferric) is even attenuated better than pH in every case. At the other extreme are manganese and calcium, which show poor attenuation by any sorbent. Lack of calcium attenuation is not surprising, since calcium carbonate is being dissolved to neutralize the acidity. Manganese is different and variable. Normally it is not attenuated well, but occasionally it is attenuated excellently and, often with soils, is even released in greater quantities than have already been released by the coal waste! (An explanation for the releases is given in the section on "Pollutant Attenuation and Movement through Soils.") The best manganese attenuation occurred at high alkalinity (pH > 11) and high cation exchange capacity (e.g., montmorillonite with a value of 115 - see Table IX). Acidity control (pH) is by far the dominant means of controlling trace elements by codisposed sorbents. Coprecipitation of less pH-sensitive elements is possible. Individual sorbents do appear to have differing, second-order abilities to attenuate elements, but the second-order effects are not readily seen for most materials. The excellent attenuation of Ni, As, and Fe++ by peat, which only raises the pH to 4.0, is a good example. Manganese attenuation by montmorillonite is another. All sorbents with any neutralizing capacity and complexing ability have some attenuating ability.

Codisposing sorbents with coal preparation wastes to moderate the dump is attractive. Except where large volumes of the sorbent are already being moved (e.g., fly ash and overburden), transporting the sorbent may be prohibitive. Extensive mixing of such large quantities will be tedious, if not impractical.

TABLE IX

ATTENUATION OF TRACE ELEMENTS IN COAL WASTE LEACHATES BY FUELS AND PROCESS WASTES

Material	Sample No	Material Parameters					Degree of Attenuation*													
		Carbonate[b] (%)	pH[c]	CEC[d] (meq/100g)	Clay[e] (%)	OM[f] (%)	pH	Fe	Al	Zn	Ni	Co	As	Fe(II)	Cr	F	Cd	Cu	Mn	Ca
Peat	25	2.2	[illegible]	18.[illegible]	[illegible]	80.0	FF	EEEE	EEEE		EEEE		EEEE	EEEE		GG			P	
NM Coal	26	1.6	7.0	[illegible]	8.1	[illegible]	GG	EEEE	GG		GG		EEEE	EEEE		GG			FF	
ProcessResidue																				
$CaCO_3$	27	60	7.4				EEEE	EEEE	EEEE	EEEE	EEEE	GG	EEEE		GG	EEEE	GG	GG	EEEE	P
Quarry Limestone	28	60	7.5				EEEE	EEEE	EEEE		EEEE		EEEE	GG		GG			EEEE	
FGD Sludge	29	90	[illegible]	[illegible]	[illegible]	[illegible]	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE		GG	GG	FF	FF	FF	P
Coal Ash Economizer	30	1.7	12.[illegible]	[illegible]	9.4	[illegible]	EEEE	EEEE	EEEE		EEEE		GG	EEEE		GG			EEEE	
Coal Ash Precipitator	31	1.2	11.2	[illegible]	[illegible]	[illegible]	EEEE	EEEE	EEEE	EEEE	EEEE	GG	FF		P	GG	GG	FF	EEEE	P
AMD Treatment Sludge	32	51.9	7.7	0.8	5.4	0.4	EEEE	EEEE	EEEE	GG	EEEE	GG			GG	FF	P	GG	GG	[illegible]
FGD Sludge	33	25.4	8.0	1.4	1.9	[illegible]	EEEE	EEEE	EEEE		GG		GG	EEEE		GG			P	
Coal Ash Precipitator	34	0.6	12.4	[illegible]	[illegible]	[illegible]	EEEE	EEEE	EEEE		GG		GG	EEEE		GG			P	
Coal Ash Bottom	35	0.7	8.[illegible]	2.8	1.0	0.4	EEEE	EEEE	EEEE	GG	FF	FF			GG	P	FF	P	P	
Coal Ash Slag	36	0.12	4.2	[illegible]	0.8	[illegible]	FF	P	FF	P	P	P			GG	P	P	P	P	P
Coal Ash Bottom	37	0.30	[illegible]	4.[illegible]	[illegible]	[illegible]	FF	FF	P		P		P	P		P			P	

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*EEEE = >100x Reduction
GG = 10-100x Reduction
FF = 3-10x Reduction
P = 0.5-3x Reduction
o = >2x Increase
[b]Carbonate by Rapid Titration
[c]pH on Filtrate from Solid Water Equilibration
[d]Cation Exchange Capacity by Ammonium Acetate Sat.
[e]Clay by Pipet Sedimentation
[f]Organic Matter by Walkley-Black Method

TABLE X

ATTENUATION OF TRACE ELEMENTS IN COAL WASTE LEACHATES BY SOILS AND CLAYS

		Material Parameters					Degree of Attenuation*													
Soil	Sample No	Carbonate[a] (%)	pH[b]	CEC[c] (meq/100g)	Clay[d] (%)	OM[e] (%)	pH	Fe	Al	Zn	Ni	Co	As	Fe(II)	Cr	F	Cd	Cu	Mn	Ca
Il Alluvium	1	1.6	8.[illegible]	8.1	17.[illegible]	0.7	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE		GG	EEEE	EEEE	GG	FF	P
Il Organic	2	6.8	8.1	[illegible]	28.6	[illegible]	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE		GG	EEEE	GG	GG	FF	o
Il Glacial Till	3	7.1	7.9	14.[illegible]	28.6	0.1	EEEE	EEEE	EEEE				EEEE	EEEE		GG			o	
Ky S12 Overburden	4	1.4	7.8	[illegible]	8.5	1.2	EEEE	EEEE	EEEE		GG		EEEE	EEEE		GG			o	
Ky S11 Overburden	5	3.8	7.6	6.8	0	1.2	EEEE	EEEE	EEEE		GG		EEEE	EEEE		GG			o	
Il Glacial Till	6	15.1	8.2	9.1	11.[illegible]	0.4	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE	GG		GG	GG	GG	GG	GG	P
Il Loess	7	8.1	8.2	8.8	9.5	0.5	EEEE	EEEE	EEEE	EEEE	EEEE	EEEE	GG		GG	GG	GG	GG	FF	P
Il Glacial Till	8	0.30	7.9	28.0	17.0	0.3	EEEE	EEEE	EEEE	EEEE	EEEE	GG	GG		GG	EEEE	FF	FF	o	o
Il Glacial Till	9	7.7	8.5	14.[illegible]	21.0	0.2	EEEE	EEEE	EEEE	EEEE	GG	GG			GG	FF	GG		GG	P
Il Glacial Till	10	13.4	8.2	[illegible]	16.1	0.9	EEEE	EEEE	EEEE	EEEE	GG	GG			GG	FF	GG		FF	P
Il Glacial Till	11	9.2	8.2	7.6	15.4	0.2	EEEE	EEEE	EEEE	EEEE	GG	GG			GG	FF	GG		FF	P
Il Glacial Till	12	8.6	8.[illegible]	8.3	20.4	0.9	EEEE	EEEE	EEEE	EEEE	GG	GG			GG	FF	GG		FF	P
Il Loess	13	5.8	8.1	11.6	12.5	0.4	EEEE	EEEE	EEEE	EEEE	GG	GG			GG	FF	GG		FF	P
Il Loess	14	0.72	7.6	14.1	35.1	0.1	EEEE	EEEE	GG	GG	GG	FF				o	FF		P	P
Il Alluvium	15	0.24	7.7	25.[illegible]	32.1	0.6	GG	EEEE	FF	o	FF	FF			P	P	P		P	P
Il Loess	16	0.48	4.8	24.1	22.1	1.[illegible]	FF	EEEE			P		GG	GG		FF			o	
Il Loess	17	0	5.6	27.9	35.9	0.5	FF	EEEE	P	P	P	FF				P	P		P	P
Ala Soil	18	0	4.0	20.5	44.7	0.3	FF	GG	P	P	P	P			GG	P	P	P	o	P
Il Loess	19	0.45	8.0	9.8	10.8	0.2	FF	FF	P	P	P	P	FF	FF	GG	P	P		o	P
Clay																				
Montmorillonite	20	0.54	7.7	115.2		0	EEEE	EEEE	EEEE	EEEE	EEEE	GG	EEEE		GG	GG	GG	GG	EEEE	P
Il Kaolinite	21	0.48	8.2	21.1		0.1	EEEE	EEEE	EEEE	EEEE	EEEE	GG	EEEE		GG	GG	GG	FF	GG	o
Montmorillonite	22	0.66	7.9	63.[illegible]		0.2	EEEE	EEEE	FF	GG	GG	GG			GG	GG	FF	FF	GG	FF
Illite	23	2.4	8.1	17.1		0.8	EEEE	EEEE	GG	FF	GG	GG			GG	P	GG	GG	GG	o
Kaolinite	24	0	4.[illegible]	2.1		0.1	FF	GG	P	o	P	P			FF	P	o	o	o	P

*EEEE = >100x Reduction
GG = 10-100x Reduction
FF = 3-10x Reduction
P = 0.5-3x Reduction
o = >2x Increase

[a]Carbonate by Rapid Titration
[b]pH on Filtrate from Solid-Water Equilibration
[c]Cation Exchange Capacity by Ammonium Acetate Sat.
[d]Clay by Pipet Sedimentation
[e]Organic Matter by Walkley-Black Method

TABLE XI

TRACE ELEMENT ATTENUATION BY SORBENTS CAPABLE OF CONTROLLING COAL WASTE ACIDITY

Attenuation	Elements
Excellent	Fe^{+++}, Al, (Zn)
Good to excellent	Zn, Ni, Co, As, Fe^{++}
Fair to good	Cr, F, Cd, Cu
Poor	Mn, Ca

D. Treating the Waste Effluent

The third option in our environmental control strategy is the collection and treatment of the polluted water that is discharged from the disposal site. Having a polluted effluent in hand makes it amenable to a variety of proven water treatment methods. We reported details on a number of these in our third annual report (LA-7831-PR). A partial listing includes

- Alkaline Neutralization
- Reverse Osmosis
- Biological Treatment
- Freezing and Distillation
- Ion Exchange
- Chelation and Precipitation
- Sorption on Solids.

Because the methods treat only a small portion of the potential polluting capacity of the waste, their strong points are economics (especially for alkaline neutralization) and effectiveness. (See the section on "Economics of Pollution Controls for Coal Preparation-Combustion Scenarios.") Several, such as reverse osmosis and ion exchange, only concentrate the pollutants, however, and must also include another step, such as alkaline neutralization. Based on effectiveness, economics, and ease of implementation, alkaline neutralization appears to be the most favorable environmental control for effluent treatment.

Alkaline neutralization with lime is a state-of-the-art method. Examining the list of natural and waste materials in Table VIII, we find that only limestone (calcium carbonate) is likely to compete with lime in a mechanical device. Even here, extensive research and development has shown that the inability of limestone to achieve high pH values (>7) severely limits the oxidation rate of ferrous ion and precipitation of manganese and hence the usefulness of limestone by itself (see R. C. Wilmoth, "Combination Limestone-Lime Neutralization of Ferrous Iron Acid Mine Drainage," EPA-600/2-78-002, Jan 1978). Lime-limestone appears to work but becomes less applicable as the ferrous iron content increases (ibid.). This statement was made for solutions with 200-500 ppm of Fe++. Coal waste effluents from the more acid-producing wastes may contain iron levels of 3000-15000 ppm of which most is Fe++. Only a high-lime-content neutralization process appears suited for these coal waste effluents.

A careful evaluation of how well and at which pH values lime cleanses coal-waste effluents of trace elements is needed to determine optimum neutralization treatments. Reliable data are also needed to determine how well these systems are described by computer codes, which give thermodynamic treatments of aqueous, ionic solutions. We have conducted a series of experiments in which a highly contaminated coal waste leachate was neutralized with lime and filtered under argon. (Experimental details and results are given in Appendix F). All 14 elements studied, except calcium and, to some extent, fluorine (not shown) are pH sensitive (see Fig. 11). Trivalent ions (ferric and aluminum) are well-known to be quite sensitive to pH changes at high acidity and behave accordingly. The attenuation of arsenic and chromium (not shown) at such high acidities is somewhat surprising. Cadmium, cobalt, copper, nickel (shown), and zinc exhibit similar behavior as a group and are greatly reduced by the time pH 7 is reached. The reason for the well-known problem of attenuating ferrous and manganese ions below pH 8 is clearly evident.

The best control technology for handling the trace element pollution in coal-preparation waste drainages is acidity control. Once the pollution occurs, pH adjustments are effective if the effluent can be collected. Given a choice, however, prevention would seem a better overall alternative.

E. Combined Pretreatment and Codisposal

An extensive experiment designed to demonstrate this disposal method is described in Appendix G. Briefly, a highly acidic, Illinois Basin coal waste was mixed in plastic 55-gal. barrels with wet slurries containing lime in amounts from 0.17% to 3.3% of the waste by weight (see Fig. 12A). In one case, 1.1% limestone in a slurry was mixed in after 0.33% lime had been used. These slurries were screened to remove excess water (see Fig. 12B) and then placed in specially designed disposal boxes (see Fig. 12C). Six boxes of each of the six lime/limestone/waste mixes were then placed in a pattern to await rain and dry weathering cycles (see Fig. 12D).

Simulated weathering cycles consisted of Monday (i.e., once a week) "rains" of 0.75 in, the equivalent of 39 in./yr. These rains drained through the treated wastes and were collected after a 24-h percolation period. Analyses for pH, iron species, and conductivity were done immediately. Sample aliquots were acidified and stored for trace element analyses.

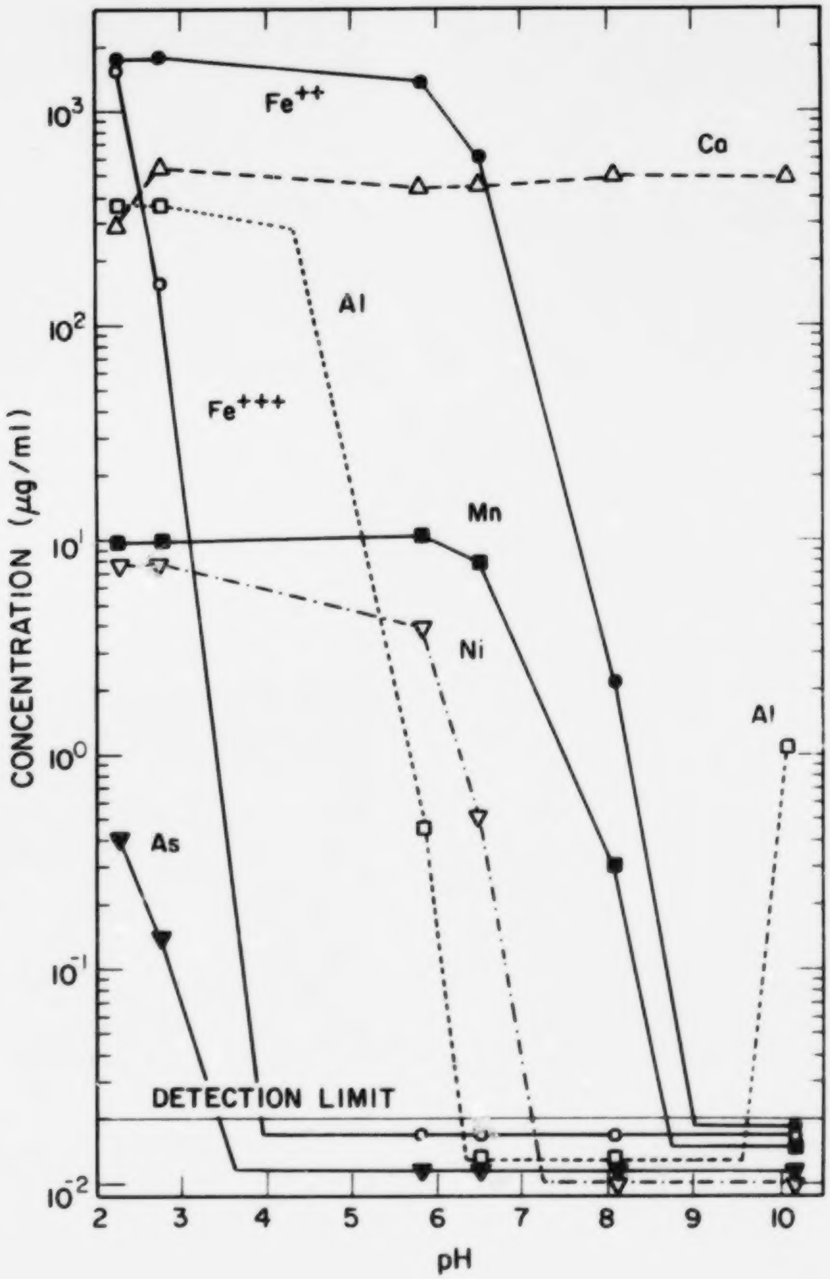
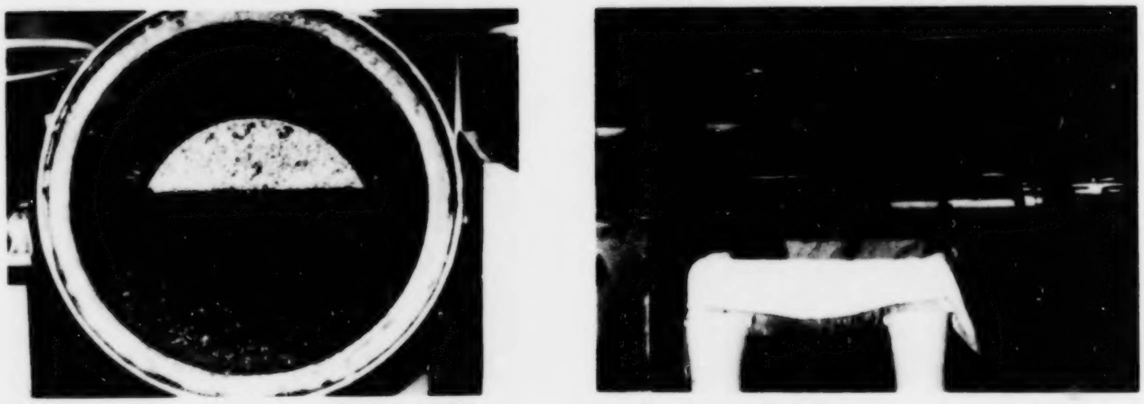
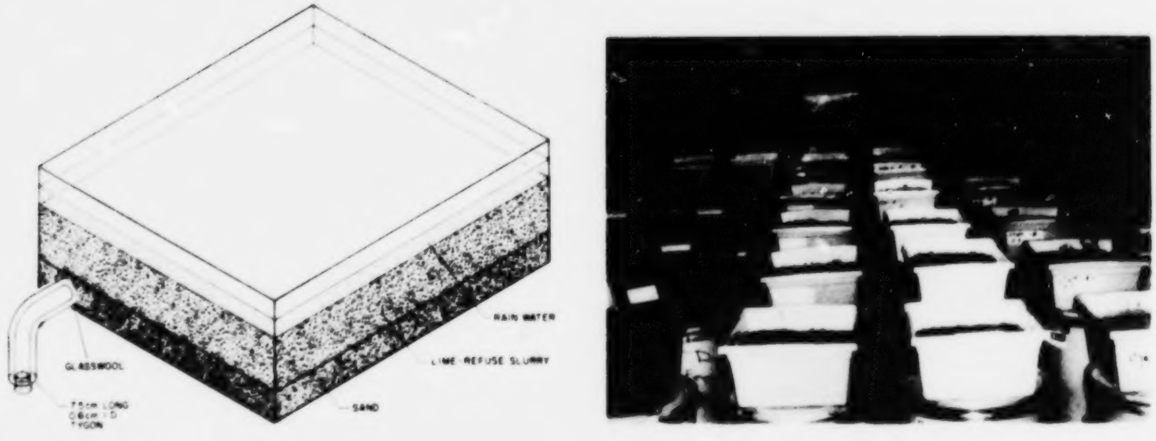


Fig. 11.
Trace element concentrations in coal waste leachate at various pH values. (Reactions run under argon.)



A
Slurry mixing

B
Slurry screening


RAIN WATER
LIME REFUSE SLURRY
SAND
GLASSWOOL
7.5cm LONG
0.6cm I.D.
TYGON

C
Disposal Box

D
Box matrix for weathering

Fig. 12.
Stages in laboratory demonstration of lime/limestone/coal waste disposal method.

All the neutralizing agent levels used (0.17% and up) were able to elevate the initial pH of the coal waste leachates above 5 (see Fig. 13).

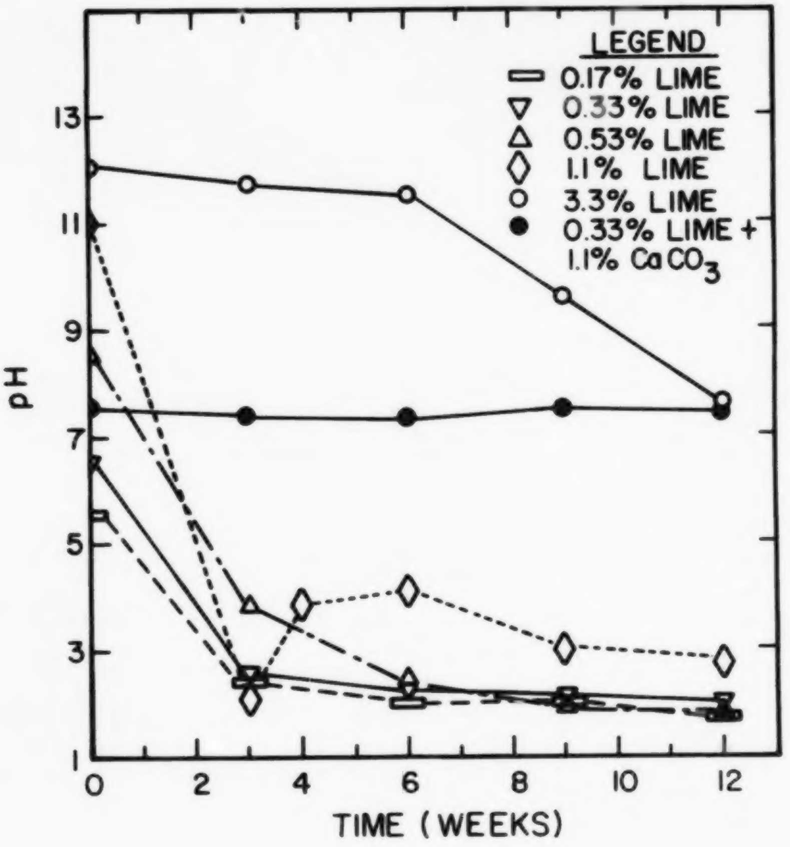


Fig. 13.
Leachate pH from lime/limestone/coal-waste mixes weathered weekly in open disposal boxes.

The two highest lime levels made the waste leachates very alkaline (pH >11), while the lime/limestone treatment gave a moderate pH of 7.6. The leachate pH values for all the lime-treated wastes except that with the highest lime content dropped rapidly. The high salt loads in the leachates from the 1.1% and 3.3% lime treatments at the 3-week mark compared to those of the lime/limestone treatment (see Fig. 14) suggest that part of this drop resulted from washing the lime out of the lime/waste systems. The lime/limestone/waste system maintained constant pH and conductivity levels for the entire 3 months monitored.

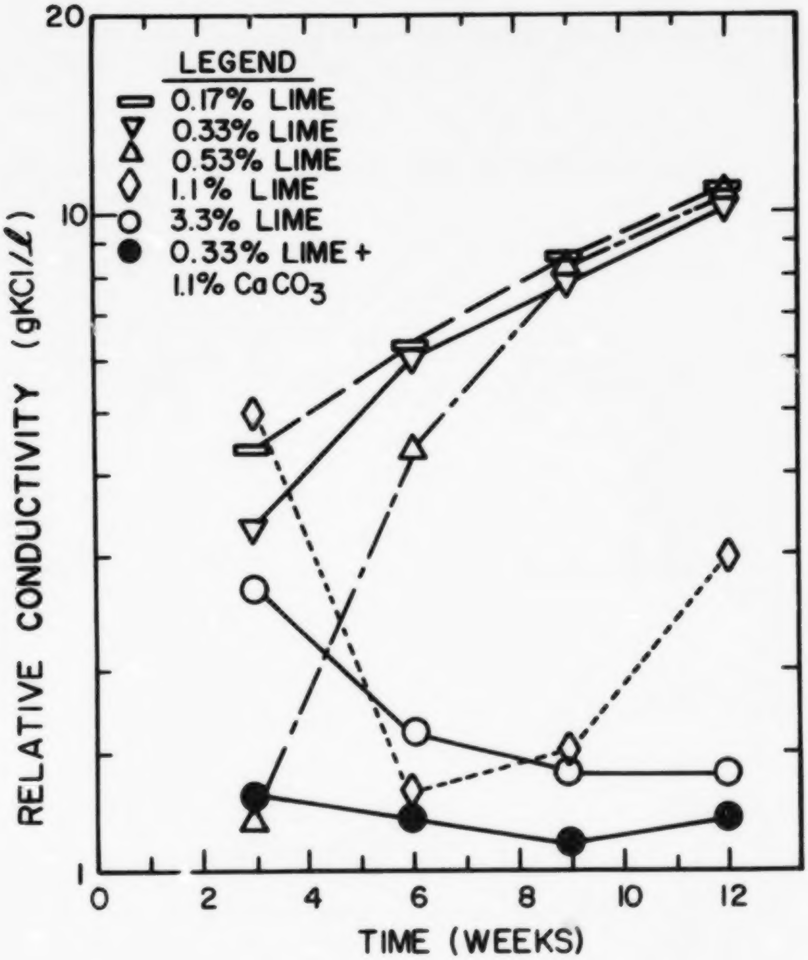


Fig. 14.
Conductivity of leachates from lime/limestone/coal-waste mixes weathered weekly in open disposal boxes.

Reduced alkalinity and pyrite oxidation combine to lower the pH and release iron when low levels of lime are present (see Fig. 15). Again the equivalent lime/limestone/waste system maintained constant pH and conductivity levels for the entire 3 months monitored.

The lime/limestone/waste system of disposal looks very good so far. it is stable for at least 3 months under some of the worst conditions (damp, open to air, and in a thin 3-1/2-in. layer) that are likely to occur in a coal waste dump. This should allow a disposer to add new layers of waste or soil on top. As the pile grows the interior will become oxygen deficient. Reductive conditions, enhanced by residual coal, will return, and the oxidized pyrite should ultimately return to pyrite.

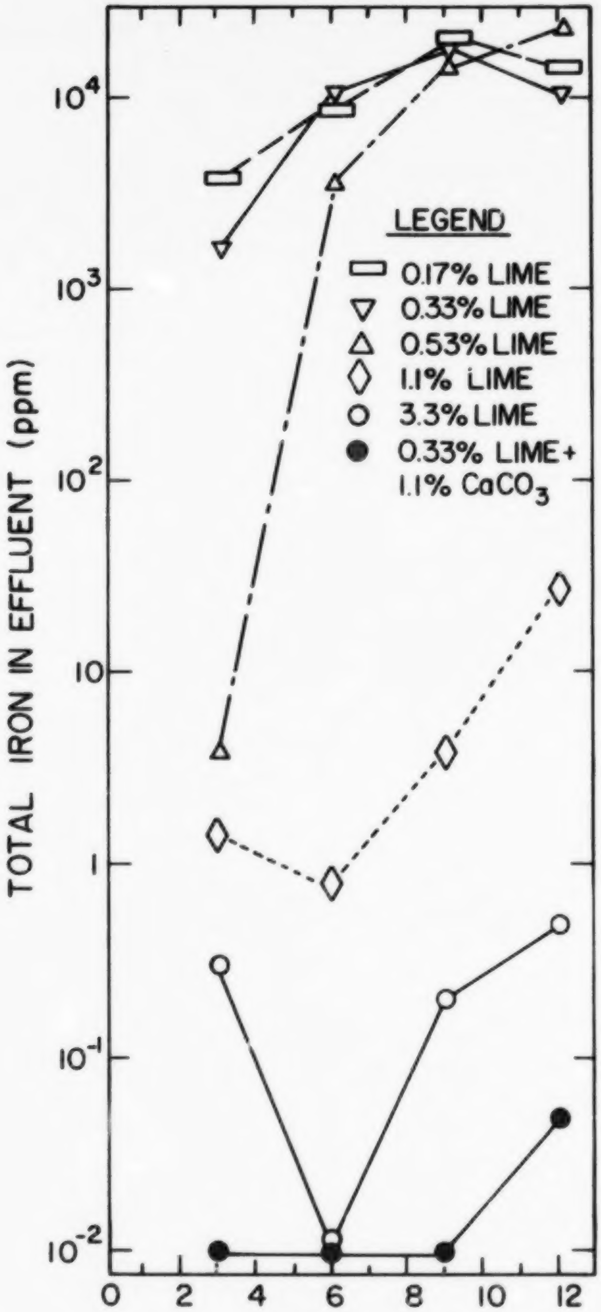


Fig. 15.
Total iron levels in leachates from lime/limestone/coal-waste mixes weathered weekly in open disposal boxes.

F. Economics of Pollution Controls for Coal Preparation-Combustion Scenarios

The economics of 10 alternative methods for preventing or treating trace element releases from coal preparation wastes have been calculated and combined with the cost of meeting pollution standards at power plants. Details about the included controls and how the economics were determined were reported in LASL document LA-8039-MS, "Costs of Coal and Electric Power Production - The Impact of Environmental Control Technologies for Coal Cleaning Plants," by E. F. Thode, J. M. Williams, E. M. Wewerka, and P Wagner (1979), and in Annual Report No. 3 of this series. The brief summary presented here covers the cost of each control method singly and combined with FGD control cost at the power plant and accounts for the compositions and volumes of wastes generated by real plants whose depth of cleaning vary widely.

Costs of 10 control technologies for three Illinois Basin preparation plants cleaning high-sulfur coals are presented in Table XII. The high-cost methods involve either extensive treatment of the waste (calcining)

TABLE XII

COSTS OF VARIOUS OPTIONS FOR CONTROLLING POLLUTION FROM COAL CLEANING WASTES[a,b]

Process	Plant A	Plant B	Plant C
Calcining - Conventional FGD	8.30	3.40	9.89
Codisposal with Fly Ash	5.84	2.62	7.71
Codisposal with Fly Ash-modified with limestone	3.90	1.75	5.15
Calcining-Lime/Limestone Recycle System	3.36	1.39	3.99
Codisposal with Alkaline Soil	1.27	0.57	1.69
Direct Addition of Lime to Pile[c]	1.01	0.45	1.33
Lime-Limestone Slurry Coating	0.50	0.22	0.44
Effluent - Ion Exchange			0.38+[d]
Effluent - Reverse Osmosis			0.26+[d]
Effluent - Lime	0.13	0.42	0.066

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[a] Actual plants; non-process in plant figures.

[b] $/ton of product coal, March 1978 time base.

[c] Labor cost not included.

[d] Cost to dispose of sludge not included.

or hauling low alkaline content fly ash. The intermediate cost methods utilize lime or locally available alkaline soils in treating the waste. The low-cost methods treat the effluent from the waste pile. The differences in the costs among the noneffluent treatment methods from plant to plant are related to the amount of waste produced by each plant and the amount of sulfur in the waste. An inspection of Table XIII shows that Plant B produces about one-third as much waste as Plants A and C per ton of clean coal and that the waste from Plant C has the highest sulfur content. The effluent treatment processes reflect the differing responses of the wastes to weathering. Plant B weathers more rapidly and produces such a concentrated leachate that we have determined that effluent treatment for it is not the cheapest process.

TABLE XIII

SULFUR LEVELS AND CLEANING YIELDS FOR THREE ILLINOIS BASIN COAL CLEANING PLANTS

	Plant		
Plant Parameter	**A**	**B**	**C**
Sulfur in Raw Coal (%)	3.7	3.9	5.2
Sulfur in Clean Coal (%)	2.8	2.8	3.6
Ash in Raw Coal (%)	30.0	18.8	29.0
Sulfur in Waste (%)	9.8	13.9	15.7
Cleaning Plant Yield (%)	68	87	72
Tons waste/ton clean coal	0.47	0.15	0.39
Tons clean coal/ton waste	2.1	6.7	2.6

The overall impact of coal usage controls, determined by adding the costs related to stack emissions cleanup at the electric power plant, is seen in **Table XIV**. For high-sulfur coals of the type discussed here, the stack controls cost in the range of \$8.50 - \$9.50 per ton of clean coal in FY-1978 dollars. Coal preparation waste controls will add less than 10% to costs with the cheaper methods and 100% or more with the more costly ones. Estimates based on 1979 prices suggest that this will add \$0.002 - \$0.004/kWh or less for the less expensive control methods for coal preparation wastes. The cost of producing electricity by coal-fired plants would seemingly be little affected by using an inexpensive control method for mitigating the effects of coal-cleaning waste on the environment.

TABLE XIV

COMBINED CONTROL TECHNOLOGY COSTS TO MEET WATER QUALITY STANDARDS AT THE CLEANING PLANT[a] AND STACK EMISSION STANDARDS AT THE POWER PLANT

	Cost of Cleaning Option & FGD, $/ton[b]		
Process	**Plant A**	**Plant B**	**Plant C**
Calcining - Conventional FGD	16.86	12.20	19.24
Codisposal with Fly Ash	14.40	11.43	17.06
Codisposal with Fly Ash-modified with limestone	12.46	10.55	14.50
Calcining - Lime/Limestone Recycle System	11.93	10.19	13.34
Codisposal with Alkaline Soil	9.84	9.38	11.04
Direct Addition of Lime to Pile[c]	9.58	9.25	10.68
Lime/Limestone Slurry Coating	9.06	9.03	9.79
Effluent - Ion Exchange			9.73+[d]
Effluent - Reverse Osmosis			9.61+[d]
Effluent - Lime	8.69	9.23	9.41

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[a] Actual plants; non-process.

[b] $/ton of coal burned, time base, March 1978.

[c] Labor cost not included.

[d] Cost to dispose of sludge not included.

II. TASK II: IDENTIFY TRACE ELEMENTS OF ENVIRONMENTAL CONCERN IN (LOW-SULFUR) COAL PREPARATION WASTE FROM THE APPALACHIAN BASIN

New samples have been collected from the Appalachian region (see Plants I and K in the section on "Waste Collection Summary"). Their evaluation has begun and will be reported next year. Complete evaluations of the low-sulfur coal waste begun last year are reported here.

A. Mineralogy and Cleaning Behavior

Low-sulfur, Appalachian coal waste differs from high-sulfur, Illinois Basin coal waste in several ways. (Data for comparison can be found for low-sulfur wastes in Appendix H and for high-sulfur wastes in the second annual report, LA-7360-PR.) The most obvious difference is the absence of pyrite (iron sulfide), corresponding to the low-sulfur content in the Appalachian coal waste studied here (see Table XV). This can readily be seen. Other minerals are comparable by x-ray analysis, but this technique accounted for only 61% of the material. Since the low-temperature ash (LTA) value is 80%, about 20% of the sample must be microcrystalline or amorphous material. Correcting the observed mineral values to approximate the LTA value (parenthetical values in Table XV) probably gives a more reasonable measure of the mineral contents. (The mineral matter in the high-sulfur waste was completely accounted for without any correction.) Thus the low-sulfur waste contains around 40% more quartz and 25% more clays (aluminosilicates). About 25% of each of these will show up in microcrystalline or amorphous states. Only a small amount of calcite, desirable for alkalinity control, is present.

TABLE XV

MINERAL COMPOSITIONS OF HIGH-SULFUR AND LOW-SULFUR COAL WASTES[a]

Mineral	Density (g/cc)	Low-Sulfur Appalachian	High-Sulfur Illinois Basin
Quartz	2.59-2.66	22.(29)[b]	21
Illite	2.7-3.0	19.(25)	14
Kaolinite	2.60-2.63	11.(14)	12
'Clays'		6.(8)	11
Gypsum	2.32	1.(2)	2
Calcite	2.71	1.(1)	2
Pyrite/Marcasite	4.95-5.17	<1.(<1)	24
Others		39.(21)	14
Low temp ash (LTA)		80	84
Non-ash (coal	<1.8	20	16

---

[a] Data in weight %.

[b] Values in parenthesis are adjusted to make minerals listed account for all of the LTA value.

The low-sulfur coal studied here was initially crushed by the preparation plant to 0 by 6 in., as were the Illinois Basin coals. The size distribution, however, was quite different (see Fig. 16). Large particles or chunks were more prominent in the high-sulfur coal wastes, whereas small particles were the norm in the low-sulfur coal waste. Although some of the differences could be attributed to the crushing machinery, a more plausible answer lies in the differences in mineral crushability. Thus, two modes should occur (as they do) in the particle size diagram: one for hard-to-crush particles (large) and one for friable particles (small). Cleat and overburden materials, together with the coal, would provide the large, starting lumps. Cleat pyrite and "rocks" would resist crushing and give higher proportions of weight to the large particles. Clays (especially dry ones) and coal would crush more easily and give higher proportions of weight to the smaller particles. (Some large particles of coal are likely because of the block cleaving of coal.) Since the density separation of two particles of similar density improves as the size of the two particles increases (our observation of raw coal buoyance), high-sulfur coals should be much more easily reduced in ash content than low-sulfur coals of similar mineral content.

Photomicrographs of the different density fractions for the low-sulfur coal waste are shown in Fig. 17. The particle density distribution of these fractions differs considerably from those of high-sulfur wastes (see Fig. 18). The lack of much high-density (> 2.97-g/cc) material in the low-sulfur waste is not unexpected, as little pyrite or other

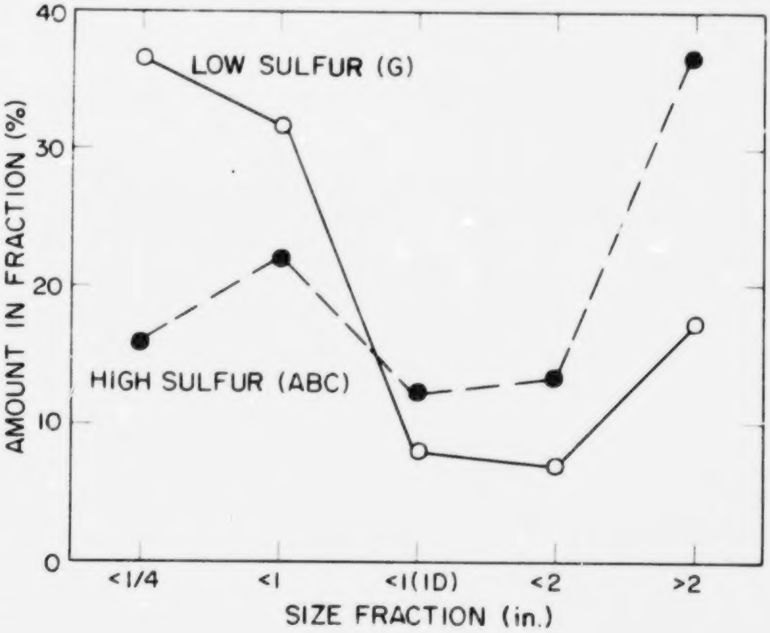


Fig. 16.

Particle size distributions of high-sulfur and low-sulfur coal wastes. (<1(1D) means <1 in. in one dimension and <2 in. in all other dimensions.

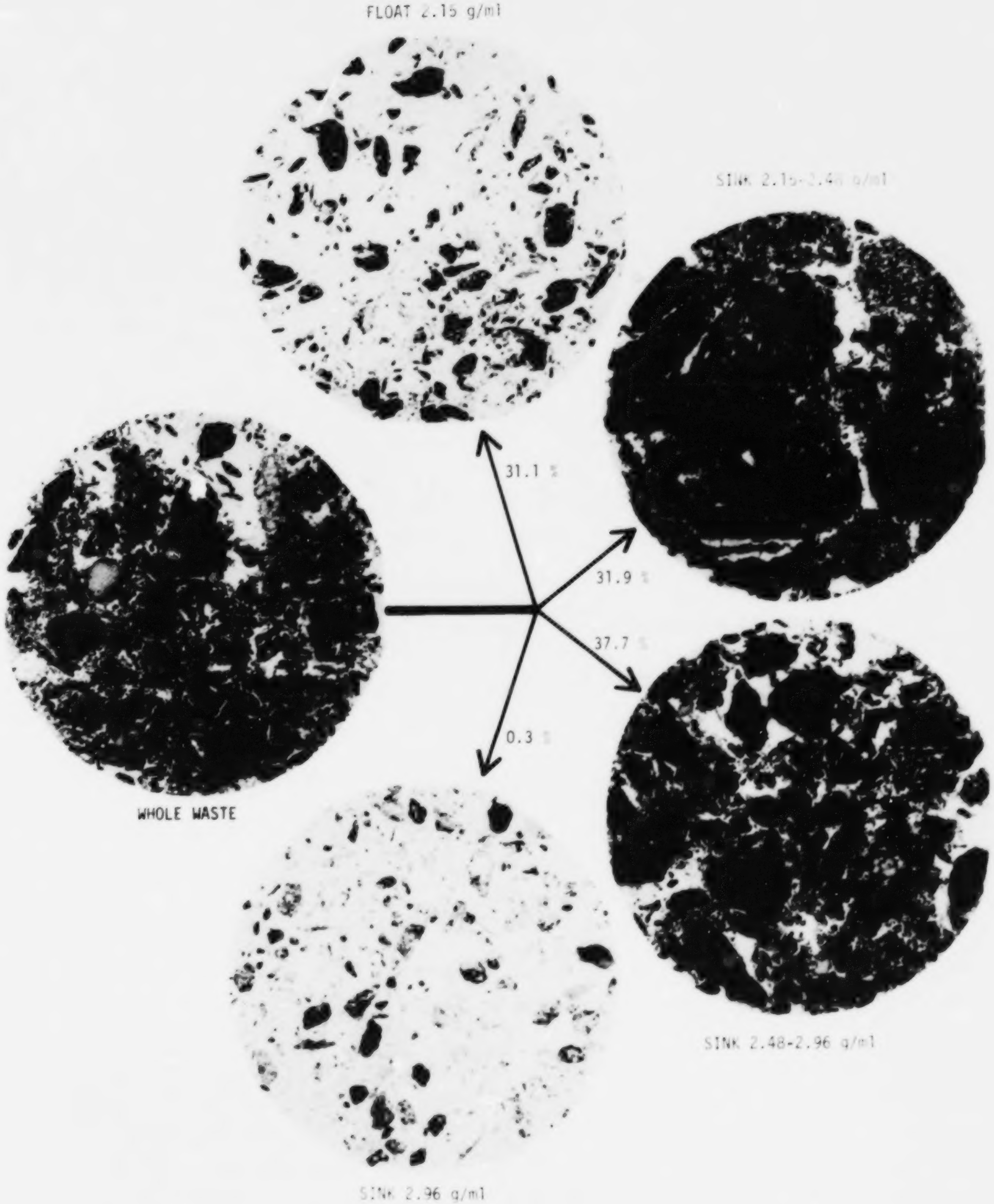

FLOAT 2.15 g/ml
SINK 2.15-2.48 g/ml
31.1 %
31.9 %
37.7 %
0.3 %
WHOLE WASTE
SINK 2.48-2.96 g/ml
SINK 2.96 g/ml

Fig. 17.
Photomicrographs of the float/sink fractions from a low-sulfur, Appalachian coal waste.

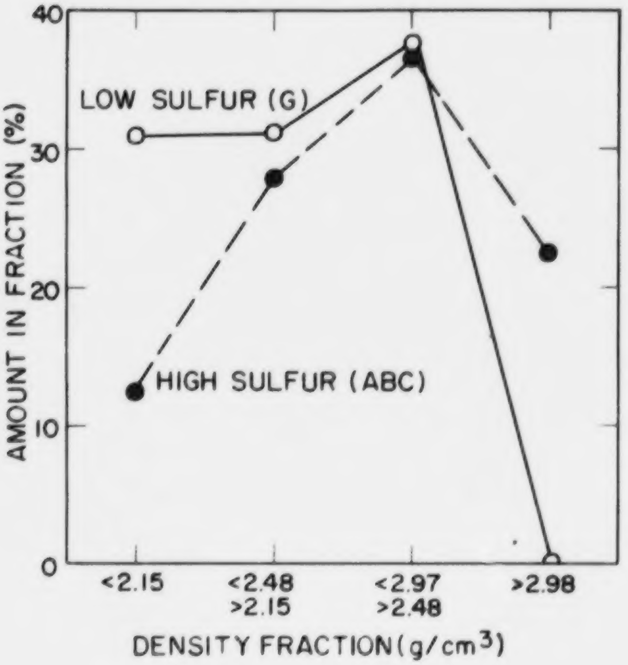


Fig. 18.
Particle density distributions of high-sulfur and low-sulfur coal wastes.

heavy-density mineral was found by x-ray analysis. The real surprise comes in the low-density (< 2.15-g/cc) fraction. Most nonsulfide coal waste minerals have densities between 2.5 and 2.97 g/cc (see Table XV). Some swelling of the expandable clays by incorporation of the organic solvent probably accounts for much of the material in the lighter 2.15-2.48-g/cc fraction. The low-density fraction, on the other hand, is mostly coal but contains half the levels of silicon, aluminum, and potassium as does the 2.15-2.48-g/cc fraction. Because few aluminosilicate particles are found by optical microscopy in the lightest fraction (see Fig. 17), the mineral components must be distributed throughout the coal particles. Cleaning these coal chunks would require extensive comminution.

B. Trace Elements and Their Locations in the Waste Structure

An important consideration in the design of control technology is the mineralogical location of the various metals that can be released. Metals in chemically immobile, inert, and unreactive minerals such as feldspars should cause no problems. On the other hand, those associated with active materials, such as pyrites and carbonates (which neutralize the acid generated by the pyrites) should be mobile.

Nearly all the elemental concentrations in the low-sulfur coal waste studied here are within a factor of 2 of those for corresponding elements in the high-sulfur wastes reported in a previous annual report (see Table XVI). Those concentrations higher in the low-sulfur waste should be

TABLE XVI

COMPARISON OF TRACE ELEMENT LEVELS IN LOW-SULFUR COAL WASTES WITH THOSE IN HIGH-SULFUR COAL WASTES

Element	Lo-sulfur	Hi-Sulfur	Ratio Lo/Hi-Sulfur	Major Element Groupings
Li	120	40	3	
Sb	2.2	1.3	1.7	
K	20000	12000	1.7	
Mg	5400	3300	1.6	
Ti	6500	4200	1.5	
Cr	93	64	1.4	
Hf	5.1	3.5	1.4	Lithophiles A
Al	92000	65000	1.4	
V	110	79	1.4	
Th	15	11	1.4	
Si	200000	150000	1.3	
Sc	16	12	1.3	
Cs	8.8	6.9	1.3	
C	3900	3200	1.2	Coal
La	49	42	1.2	
Cu	48	42	1.1	
Ga	20	18	1.1	
Zr	130	120	1.1	
Ta	1.1	1	1.1	
Dy	5.6	5.4	1.0	
Lu	0.4	0.4	1.0	
Yb	2.8	2.9	1.0	Rare Earths-Miscellaneous B
Ce	79	85	0.9	
Eu	1.3	1.4	0.9	
Be	2.5	2.8	0.9	
Cd	0.33	0.39	0.8	
Ni	49	58	0.8	
B	55	68	0.8	
Na	1300	1600	0.8	
Sm	5.3	6.8	0.8	
F	570	750	0.8	
Rb	130	180	0.7	
U	4.2	5.9	0.7	
Y	19	27	0.7	
Zn	69	120	0.6	
Pb	22	44	0.5	
Mn	97	190	0.5	Chalcophiles C
Co	11	25	0.4	
As	18	57	0.3	
Fe	20000	94000	0.2	
Ca	1400	19000	0.07	
S	7100	110000	0.06	Calcite-Pyrite-Apatite D
P	150	3400	0.04	

related to clays and quartz (lithophiles). Those higher in the high-sulfur waste should be related to sulfides (chalcophiles). Calcium, sulfur, and phosphorous, interestingly, are much lower in the low-sulfur waste. Pyrite and calcite are measurably lower (see preceding section), whereas apatite is not measurable but should be lower than in the high-sulfur waste. To define better the element and mineral relationships, we have used both statistical analyses of chemical and mineral data and scanning electron microscopy (SEM) analyses of mounted powder specimens.

Statistical analyses proved effective with high-sulfur wastes (second annual report, LA-7360-PR). In general, such analyses only give one behavioral pattern per element and require some physical separation of the various mineral species followed by accurate (±5%) chemical analyses. We used the three methods here which proved successful earlier. The first method takes advantage of the separation made at the preparation plant during the coal cleaning process. The input coal and output coal and waste streams provide a reasonably sharp separation of the mineral and coal components based on density differences. The second method is based on particle size separations before laboratory crushing and assumes that some particles, such as cleat pyrite, will resist crushing and, therefore, show up as large chunks. The third separation method is based on mineral density differences as used in conventional float/sink procedures. Our float/sink technique utilizes very small particles and many tedious separations in order to achieve the cleanest separation possible. Analytical data for these samples are given in Appendix H. A discussion of the mineral and size fractionation in the separation schemes was given in the preceding section.

Fig. 19 is a visual representation of the statistical analysis of the chemical data for the coal and waste samples as collected at the low-sulfur coal cleaning plant. (See the section on "Visual Presentation of Statistical Results" for information on how to achieve this display.) The elements fall into two well-defined groups: the smaller group has only nitrogen (N), sulfur (S), calcium (Ca), and cobalt (Co), while the other has everything else. Elements in the smaller group correlate inversely with the LTA and are more concentrated in the coal portion of the plant streams. Nitrogen appears to be the best indicator for the coal component. The major sulfur component is coal associated, although inspection of the original sample data shows that sulfur becomes concentrated in the fine waste stream in contrast to nitrogen. This implies that a second type of sulfur occurrence exists in the fine particles. Mineral sulfides would be a logical explanation for this.

Statistical treatment of the chemical data for samples produced by the particle sizing method also produce two groupings (see Appendix H). Neither was as distinct as the groupings described above. Arsenic (As), iron (Fe), copper (Cu), lead (Pb), and perhaps gallium (Ga) are found to be associated with sulfur. These elements occur in higher concentrations in the very small (<-20-mesh) and very large (>2-in) particles than in the midrange sizes. (A plausible explanation might be the occurrence of microscopic and massive forms of pyrite.) The remaining elements fall into a weakly defined group containing phosphorous (P), aluminum (Al), and silicon (Si). Of particular note are the presences of manganese (Mn), cobalt (Co), uranium (U), zinc (Zn), nickel (Ni), and possibly cadmium (Cd) in this, the clay group.

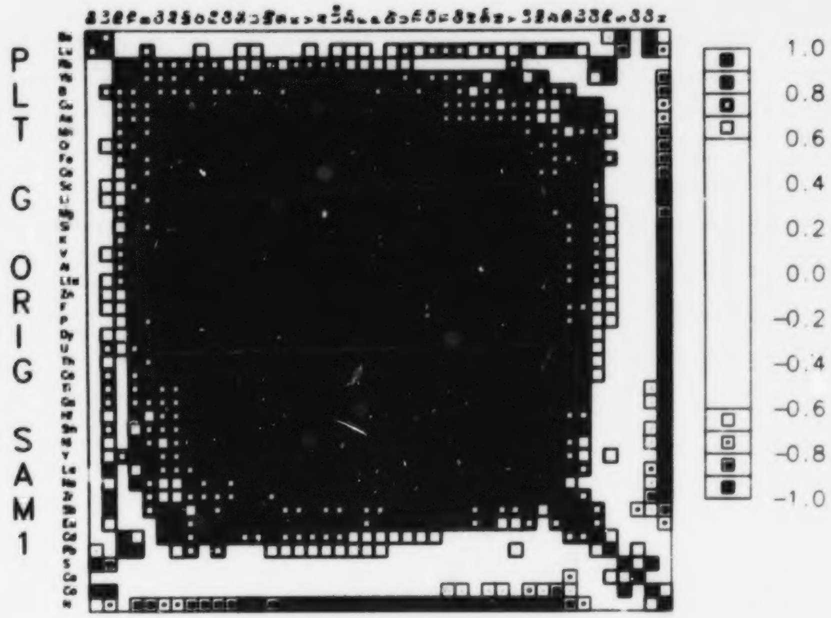


Fig. 19.
Trace-element, correlation-coefficient clusters for all coal and refuse samples collected from Plant G.

Statistical treatment and clustering of data for samples produced by float/sink separation form two distinct groups, the larger of which appears to have two, less well-defined, subsets. The subsets roughly correspond to aluminosilicate and rare earth clusters. The other distinct group corresponds to heavy mineral species, primarily sulfides.

Combining the three sets of statistical clusterings, five element-mineral association groups are obtained (see Fig. 20). All of the elements studied are shown grouped in the third row. Our best guesses as to the mineral types that these groups represent are given in the fourth row. An important consideration should be noted when viewing this table and in using statistical schemes in general; namely, only one, the dominant, behavior is seen in any separation scheme. Iron, for example, shows up in only one place (as a sulfide) when, as is clear from elemental levels and microprobe studies, it occurs in other mineral phases as well. The qualification should be that the element-element associations found are real, but that other element-mineral associations can exist and that more separation treatments, analyses techniques, or data analyses are needed to further evaluate the exact mineral location, especially when multiple mineral occurrences of an element exist.

Electron and ion microprobe techniques have the ability to single out small mineral particles and interrogate their elemental composition. Combined with the statistical techniques, they provide an excellent means of relating macro and micro information. For our own purposes, where we have been interested mainly in gross environmental behavior, we have used these microprobe techniques to verify and expand our understanding of the mineral associations of the trace elements.

Statistical Treatment	Element Groupings†					
	I	II	III	IV	V	VI
Plant Separation	N,S,Ca,Co	Others				
Sized Waste	N,S,Ca	As,Fe,Cu, Pb,Ga	Others			
Float Sink	N,S,Ca	S,As,Fe, Cu,Pb	Mn,Zn,Ni, Hf,Zr,La	Ce,Th,U,Dy,Y, Eu,Yb,Lu,B,Rb, Cr,Ti,P,Ca	Li,Cs,Sc,Al, Si,K,Na,Mg, F,Sn	Cl,Tb,Cd,Be V,Ta,Co,Ga
Best Guess Evaluation	Coal/Carbonates	Sulfides	Oxides/Carbonates (Sulfides)	Oxides/Phosphates	Clays/Quartz	Questionable but mineral

†Based on statistical treatments presented in the text
††Circles around an element indicate uncertainty;
also possible multiple mineral assignment
*Some assignments based on previous two treatments

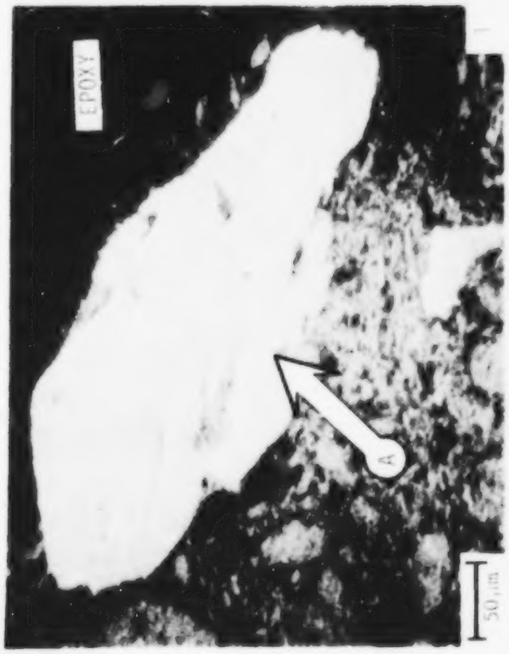
Fig. 20.
Major element associations in Plant G, Appalachian coal waste.*

The bulk of the low-sulfur waste material (Plant G) is composed of silica, aluminosilicates, potassium aluminosilicates, and coal. A photographic abridgment of the many particles studied is given in Fig. 21. Some, but not all, of the circular iron sulfide particles in Frame 3a include manganese, copper, zinc, and perhaps magnesium. These circular inclusions occur at cracks and contain aluminum and silicon as well. The rare earth elements identified in the particles in Frame 4 were cerium (Ce), lanthanum (La), and neodymium (Nd). No calcium was found. The copper sulfide particle in Frame 5 contains some zinc and iron. The aluminosilicate region in Frame 7 contains iron and manganese. In addition to these particles, massive and framboidal pyrite areas were observed. Some of the framboidal areas were backfilled with iron sulfide containing arsenic. Carbonate particles were composed mainly of calcium, magnesium, and perhaps aluminum with some manganese and iron. Iron, titanium, and zirconium oxide particles were common. Some silica particles contained high levels of iron and zirconium. Barium sulfate particles were also prevalent. In general, this waste contained a wide variety of accessory minerals in a predominantly aluminosilicate matrix.

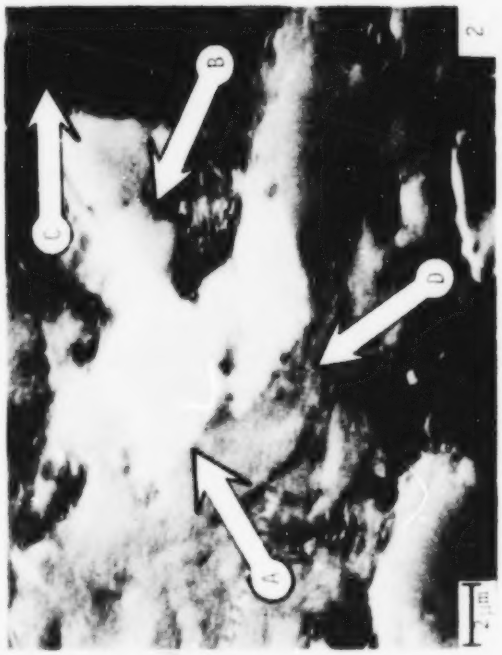
The corroborative statistical and microprobe data have allowed us to generate a list of the locations where the elements in this low-sulfur waste reside (see Table XVII). Those elements assigned to clay may actually reside as nonaluminosilicates interspersed throughout the clay. Also, many of the sulfide minerals are buried in or surrounded by clay matrices. For a comparison with the element locations in high-sulfur, Illinois Basin wastes, the reader is referred to a similar table in the second annual report (LA-7360-PR, p.26). Trace element location information is also obtained from leaching behavior.

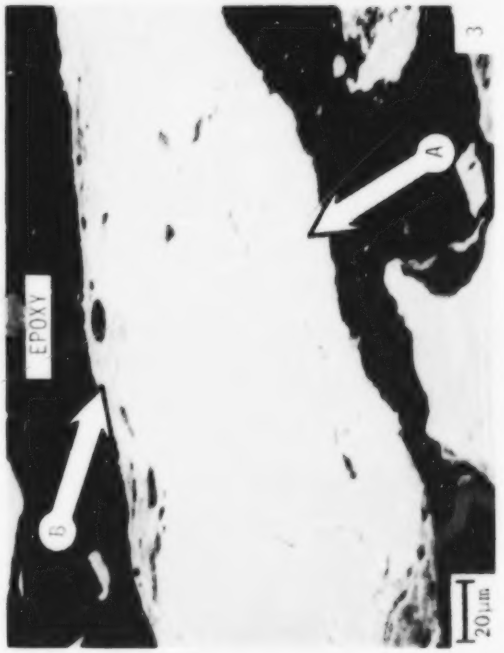
Fig. 21. (Pages 48 and 49)
SEM photographs of selected particles observed in a low-sulfur coal preparation waste.

Frame 1: Gypsum particle (A).
Frame 2: Chalcopyrite (A), silica (B), coal (C), and a KAlSi-type clay mixture (D).
Frame 3: Massive-type pyrite (A) with KAlSi-type clay (B) attached.
Frame 3A: Circular iron sulfide inclusions (A) in massive-type pyrite particle (B) of Frame 3.
Frame 4: Rare earth phosphate particles (A) with KAlSi-type clay (B). AlSi-type clay (C) also present.
Frame 5: Copper sulfide particles (A).
Frame 6: Zinc sulfide-clay particle (A).
Frame 7: AlSi-type clay region (A) merging into quartz area (B).

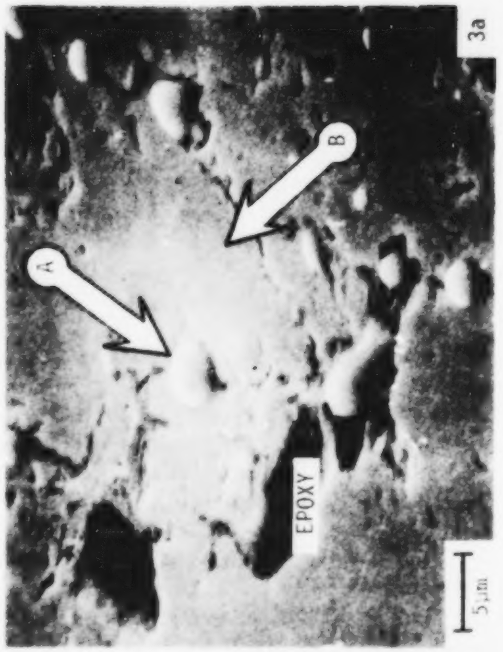

1

EPOXY
A
50 µm

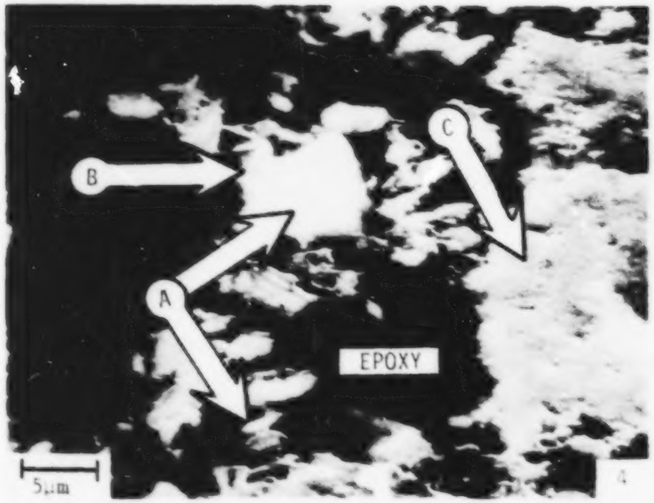

2


3

EPOXY
B
A
20 µm

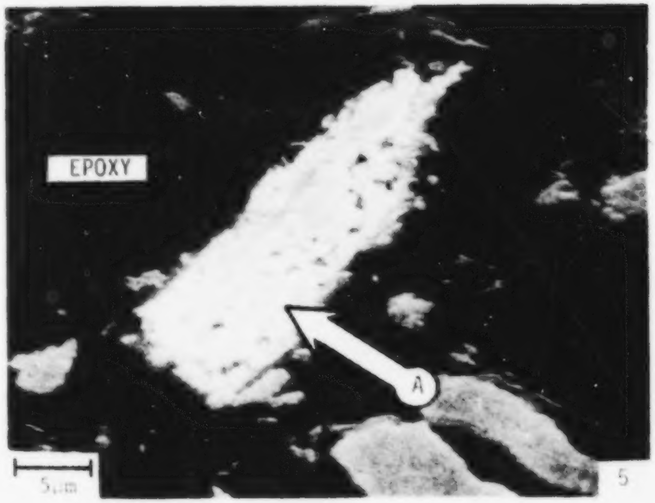

3a

A
B
EPOXY
5 µm

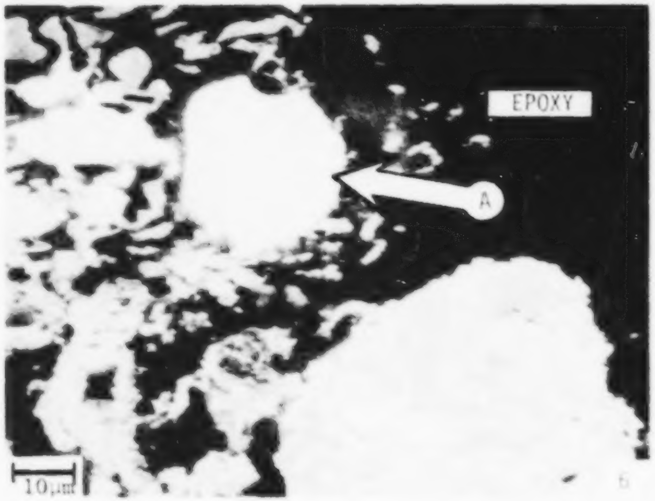


4

B
C
A
EPOXY
5µm

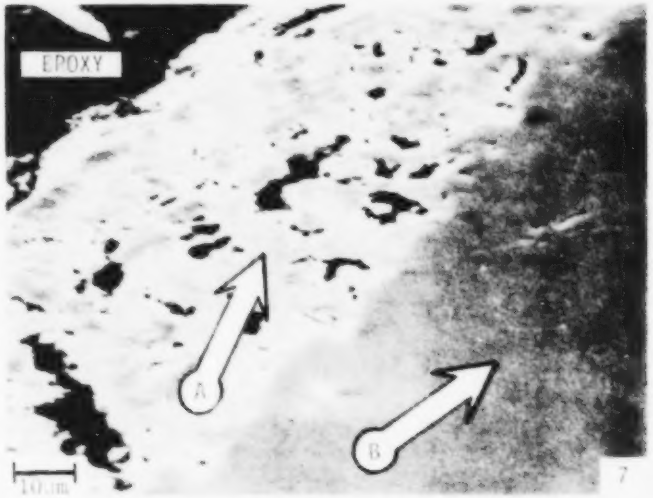


5



6

EPOXY
A
10µm



7

EPOXY
A
B
10µm

TABLE XVII

MINERAL LOCATIONS OF TRACE ELEMENTS IN A LOW-SULFUR, APPALACHIAN COAL WASTE

ELEMENT	RESIDENCE IN WASTE	ELEMENT	RESIDENCE IN WASTE
Li	Clay	Ge	???
Be	Clay	As	Sulfide
B	Clay	Rb	Clay
N	Coal	Y	Clay
F	Clay	Zr	Oxide (in clay)
Na	Clay	Mo	???
Mg	Clay, carbonate	Cd	Sulfide
Al	Clay, carbonate, iron sulfide	Sn	???
Si	Clay, silica, iron sulfide	Sb	Sulfide
P	Phosphates (in clay)	Cs	Clay
S	Coal, sulfides, sulfates	La	Phosphate
Cl	???	Ce	Phosphate
K	Clay	Sm	Phosphate
Ca	Clay, sulfate, carbonate	Eu	Phosphate
Sc	Clay	Tb	Phosphate
Ti	Oxide (in clay)	Dy	Phosphate
V	??? (possibly with iron oxide)	Yb	Phosphate
Cr	Clay (with Al)	Lu	Phosphate
Mn	Sulfide, carbonate, clay	Hf	Oxide (in clay)
Fe	Clay, sulfide, carbonate, oxide	Ta	Clay
Co	??? (possibly as sulfide)	W	???
Ni	Sulfide	Pb	Sulfide
Cu	Sulfide (w/wo iron)	Th	Clay (possibly as phosphate)
Zn	Sulfide	U	Clay (possibly as phosphate)
Ga	Mineral phase		

C. Trace Element Leachability

The behavior of low-sulfur coal preparation waste under the influence of leaching and weathering is the primary concern from the environmental point of view. To determine this behavior we have subjected composite samples from Plant G of the Appalachian region to both batch and column leaching tests. Portions of these experiments were reported in the third annual report (LA-7831-PR). Complete results are tabulated and plotted in Appendixes I and J of this report.

The trace element leaching behavior of the low-sulfur waste with time, when equilibrated with water in the presence of air, is shown in Fig. 22. A general lack of any strong time dependence over the study period (42 days) is readily apparent for most elements, although small increases in the levels of some elements over those in the initial (10-min) period were found by the 5th day. (The behaviors of Cr and Cu are clearly kinetically controlled.) A growing, upward trend for Al, Cr, Co, Cu, Fe, Mn, and Zn does seem apparent and corresponds to the increase observed in the acidity (drop in pH). This probably signals slow sulfide oxidation.

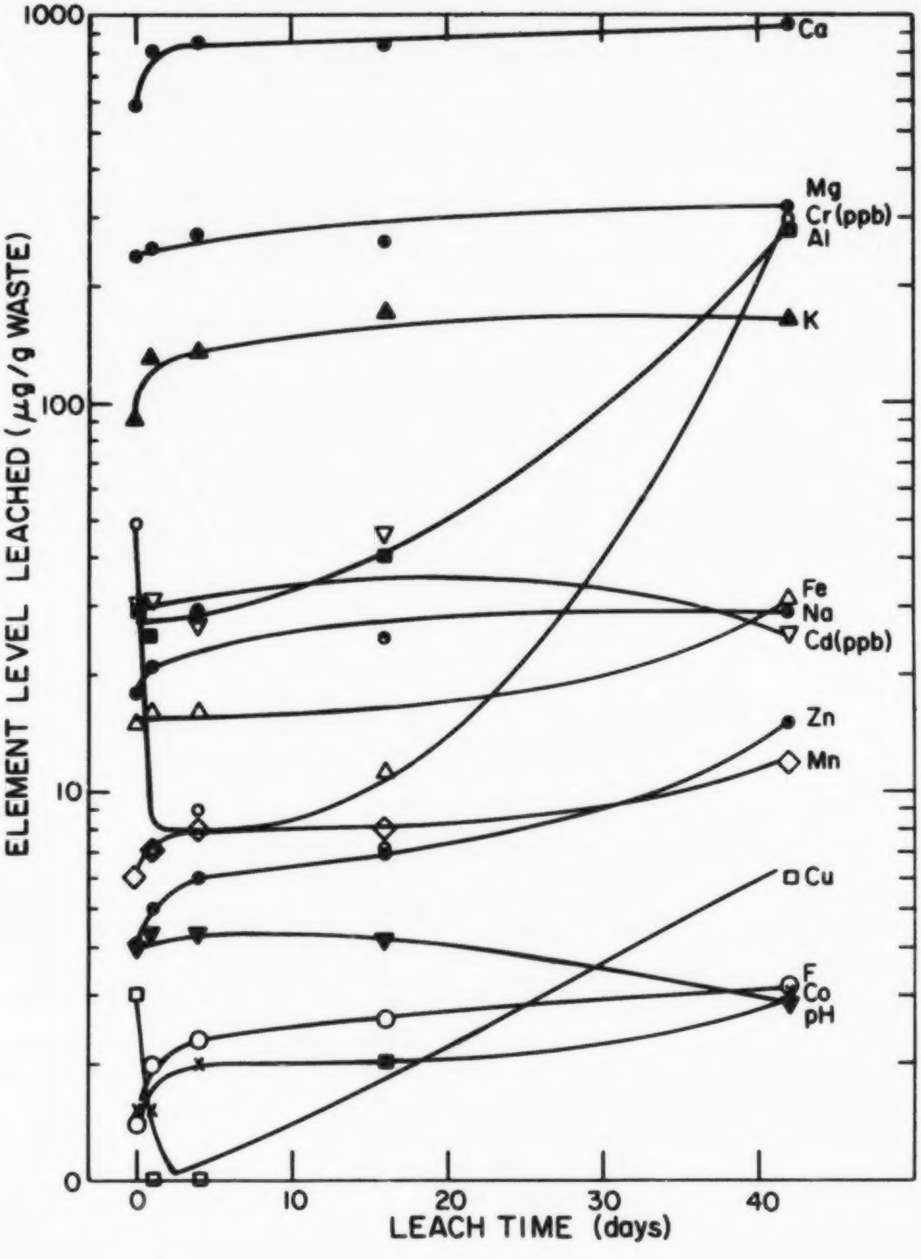


Fig. 22.
The pH and trace element levels as a function of leach time during the batch leachings of a low-sulfur, Appalachian coal waste.

The most surprising result from the leachings is the low pH values of the leachates. The initial value was 3.9. After rising quickly to 4.3, the pH was still falling when it reached 3.0 at the experiment terminus. This low pH level was unexpected for the small amount of pyrite present. The low iron values would suggest that not much pyrite was oxidized. The polluting parts of the waste may not "generate" much pollution, but what little is generated cannot be abated by the rest. This is not entirely surprising, since this waste started with little calcium, and the most readily identifiable calcium mineral was gypsum, although the presence of some calcite was identified by x-ray mineralogy (see Table XV).

The most highly leachable elements, as measured by the percentage of the total available, are Ca, Co, Cd, Ni, Zn, and Mn. This suite is the same as was found for the high-sulfur coal wastes. A comparison of the percentages leached in 1 day for the 14 elements in common between Plant G (low sulfur) and Plant B (high sulfur) is given in Table XVIII. Generally, the percentages leached are lower for the low-sulfur coal waste. Fe, Al, and Cr have much lower leachabilities for the low-sulfur coal waste. The prevalent view seems to be that high-sulfur wastes give high-iron leachates, and that low-sulfur wastes give low-iron leachates, but the situation is more complicated than this.

TABLE XVIII

PERCENTAGES OF TRACE ELEMENTS LEACHED FROM SOME COAL WASTES[a]

Element	% Leached		Ratio
	Low Sulfur[b]	High Sulfur[c]	Hi/Lo Sulfur
Ca	60	55	0.9
Co	14	100	7
Cd	9	32	4
Ni	8	41	5
Zn	7	23	3
Mn	7	16	2
Mg	5	9	2
Cu	2	14	7
Na	1.5	1.1	0.7
K	0.6	0.3	0.5
F	0.4		
Fe	0.08	5.7	70
Al	0.03	1.4	50
Cr	0.01	0.6	60

---

[a] 1 day shaker leach of 50g of -20 mesh waste with 250-ml water; room temperature, open vessel.

[b] Plant G.

[c] Plant B.

In Fig. 23 we have plotted the percentages of each element leached from the low-sulfur waste versus those from the high-sulfur waste. (The solid diagonal lines indicate the magnitude of the difference in leachability between the two sets of data.) Immediately recognizable is the clustering of the elements into monovalent, divalent, and trivalent groups (marked by dashed lines). The low solubilities for the monovalent cations deny the existence of appreciable simple salts in the waste and suggest that these elements are bound tightly in aluminosilicate structures. (Simple salts such as sodium chloride would have been removed, if they were ever present, by the washing process.) The dramatic difference in the behavior of the trivalent species* suggests that leachate acidity might be dictating their leaching response. Plots of the element levels in the leachates for the three Illinois Basin plants and the Appalachian plant show that the aluminum and iron levels change enormously with small changes in pH (see Fig. 24). The divalent elements show less sensitivity, although manganese increases with increasing acidities at low pH. The pH-associated behavior of potassium is not explained.

Since the comparisons of element leachabilities for the high-sulfur and low-sulfur coal wastes were made using data corresponding to pH 2.2 and pH 4.3 (indicated by the arrows at the bottom of Fig. 24), the high-sulfur waste is much worse than the low-sulfur waste. Comparing the low-sulfur coal waste with the high-sulfur waste from Plant A (pH 7.3), however, will show that the low-sulfur waste is worse. Over the short term (at least 8 wk), the leaching behavior is not dependent on the amount of pyrite in the coal but rather on the ability of the waste to control acidity. Natural or induced alkalinity is the critical parameter.

The batch or equilibrium experiments yielded results emphasizing constant interaction between the solid waste and the same unreplaced leachate. Column leaching experiments emphasize the interaction of a continuously changing leachate with the waste, accentuate the dissolution of readily soluble materials, and on occasion, illuminate the chromatographic behavior of transportable species through the solid being leached (see also the section on "Column (Dynamic) Leaching"). By draining the column, aerating the waste, and then reestablishing water flow, soluble species from oxidatively sensitive components are easily seen as they concentrate in the first few increments of leachate that pass through the column. Subjecting coal wastes to dynamic leaching experiments should provide additional insight into their leaching behavior and provide information about the discharge levels expected.

Column leaching experiments utilizing the low-sulfur Appalachian coal waste are described in Appendix J, where trace element levels in the leachate increments are tabulated and plotted. Plots of pH, total dissolved solids, potassium, and iron levels at various effluent volumes are also given in Fig. 25. The initial leachates from each column are more acidic (pH 2.9) than the 10-minute leachates from the batch studies (pH 4.3). This probably arises from a combination of a flow that is too fast (0.5 mℓ/h - see the section on "Column (Dynamic) Leaching" for a discussion of flow rates) and the presence of leachable material at the exit

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*Iron apparently is oxidized readily from the ferrous to ferric state in the open vessels when the pH is above 2.

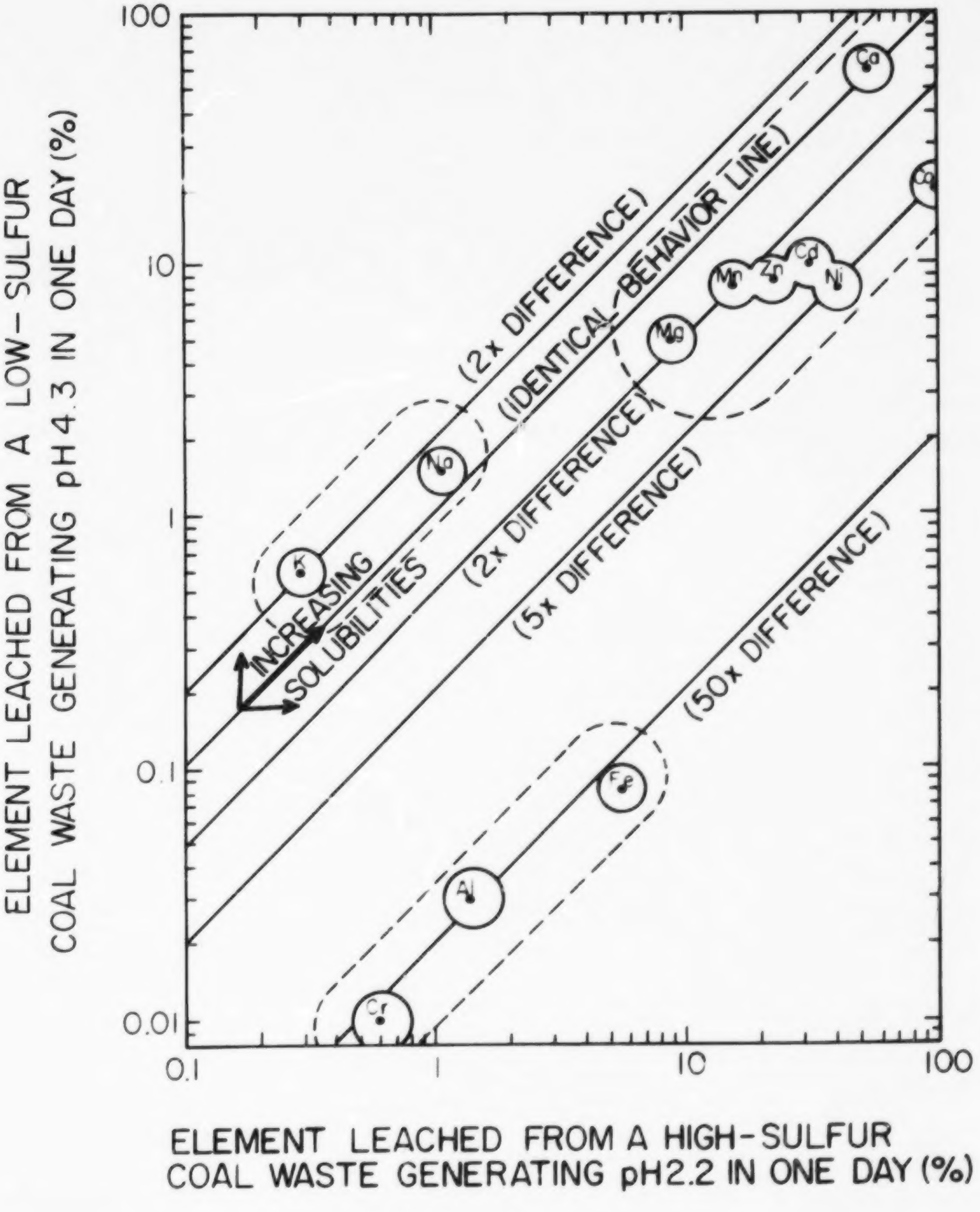

Fig. 23.
Relationships between the percentages of trace elements released from high-sulfur and low-sulfur coal preparation wastes.

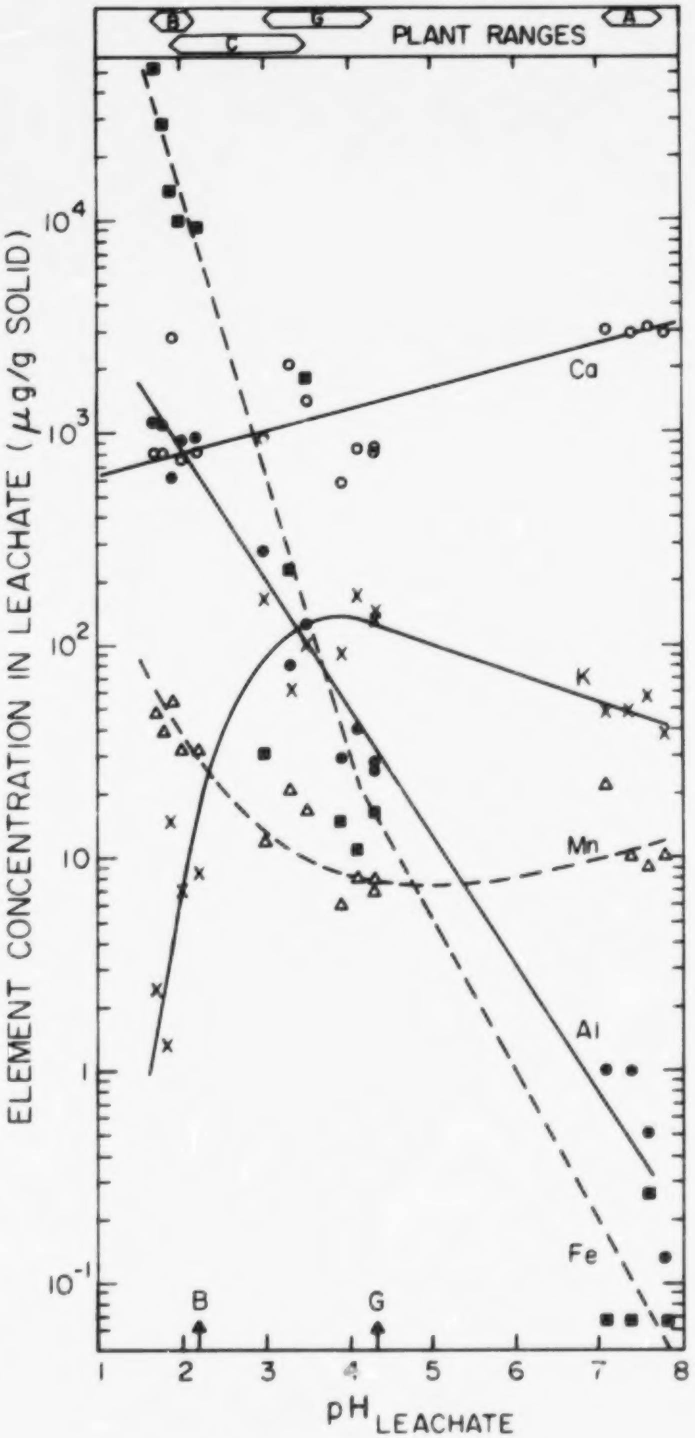

Fig. 24.
The pH-controlled release of elements into coal waste leachates. (Plants A, B, and C have high-sulfur wastes; Plant G has low-sulfur waste; Plant A has > 1% calcite present.)

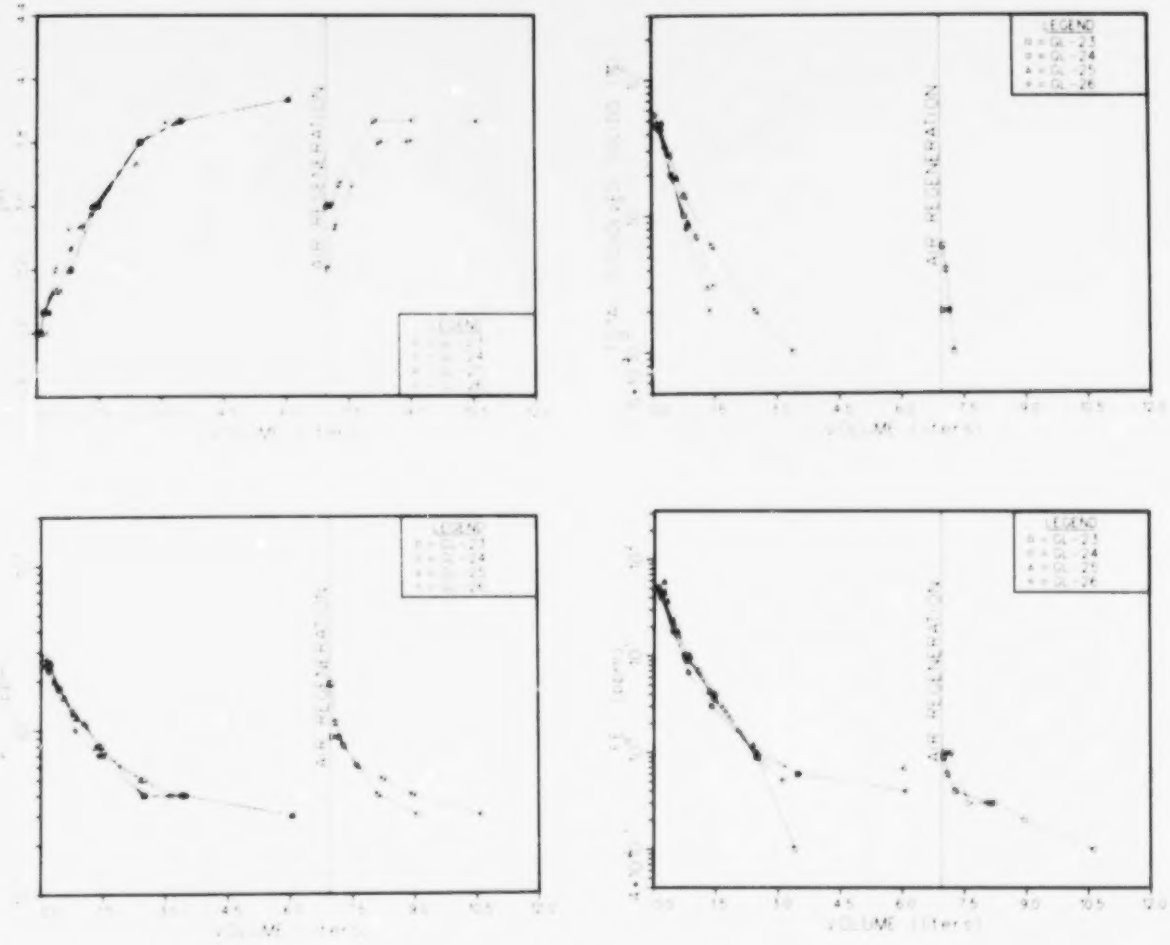

Fig. 25.
Leachate pH, total dissolved solids, and potassium and iron levels for column leachings of Plant G coal preparation waste.

boundary. Both would minimize leachate interaction with the acid neutralizers in the waters.* The pH values level off at 3.9, which is near the 1-day batch experiment pH value. Trace element concentrations in these leachates are discussed in the next section in relationship to pollution assessment.

Dissolved solids load in the column leachates is not particularly high (< 0.5 percent) and drops exponentially as the volumes of the leachates increase. Similar behavior is observed for all 14 elements measured (Al, Ca, Cd, Co, Cr, Cu, F, Fe, K, Mg, Mn, Na, Ni, and Zn), as illustrated by potassium and iron in Fig. 25. This is consistent with exponential elution (dilution) of nonregenerative species. Regenerative species are present, however, as demonstrated by the drops in pH (down to 3.2) and increase in element levels after column airing and resumption of leaching (see the level increases after the "Air Regeneration" lines of Fig. 25). They are simply not regenerated under the experimental conditions.

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*Column leaching of Plan A waste really demonstrated this behavior. Initial leachate pH was around 2.9 for the column and 7.1 - 7.8 for the entire batch time period (10 min to 56 days) - Second Annual Report (LA-7360-PR).

Like the batch leaching data, the column leaching data also contain information about the locations of the elements in the waste. Figure 26 shows the column leaching behavior of the low-sulfur coal waste. Element leaching behavior along the horizontal axis is defined by the amount of the element in the initial leachate fraction relative to its level in the waste, i.e., pseudo percentage-leached parameter. Leaching behavior along the vertical axis is defined by the level of the element in the initial fraction relative to its level in the first fraction collected after airing. Three general clusters appear. As with the batch experiments, these clusters contain only common or isovalent species. The horizontal axis indicates that only the divalent species have significant

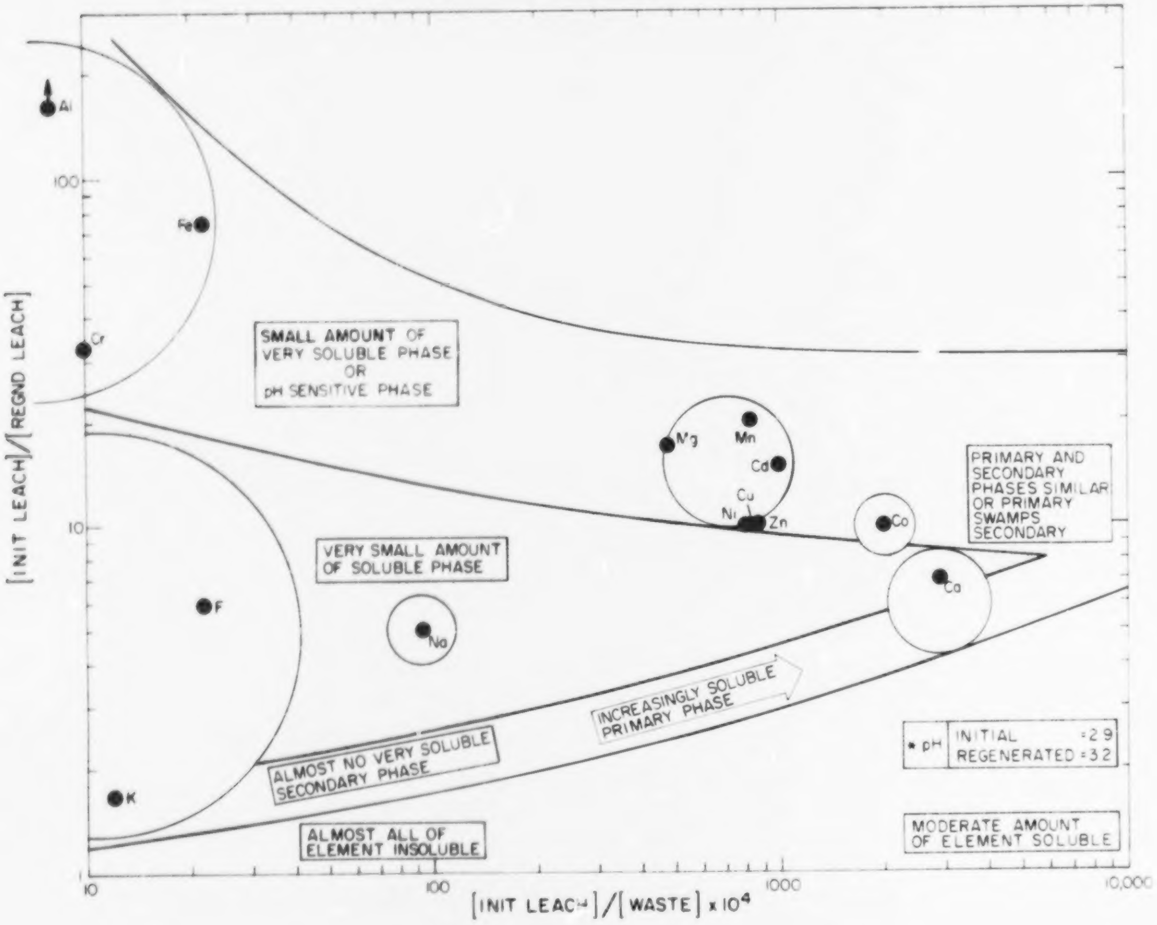

Fig. 26.

Elemental associations from the column leaching data of a low-sulfur coal waste.

solubility. The fluorine position suggests the possibility of fluoroaluminosilicates, although fluorophosphates are possible and more common. The vertical scale shows that the trivalent species had a greater amount of a soluble phase present at the beginning of the leaching than after the "air-regeneration" of the column. The divalent elements show less difference, and the monovalent elements show almost none. The higher pH (3.2) in the regenerated case than was initially encountered (2.9) could explain the difference (see the pH-dependency in Fig. 11). Alternatively, the lower initial pH could indicate that more oxidation had occurred before the beginning of the leaching than during the "air-regeneration" step. In either case, the oxidation step points to at least two phases (locations) for each of these "oxidatively sensitive" elements.

Figure 27 is a similar presentation of the column leaching data for the high-sulfur coal waste from Plant B. The general alignment is similar except for the trivalent cluster. Cr and Al have moved to a higher initial solubility. This is probably reflective of the higher acidity for this waste. Even more noteworthy is the behavior of iron. In this case, iron is more closely aligned with the divalent elements than the trivalent ones. This coincides with a major change in the occurrence of iron. Here iron resides predominantly in pyrite (ferrous or divalent state), whereas in the low-sulfur waste it occurs mainly with the clays (most likely in the ferric or trivalent state). Alternatively, the shift might simply reflect the pH-sensitivity of iron noted earlier (Fig. 11). Another cluster contains rare earth elements and uranium and reflects phosphate behavior. The "regeneration" behavior for fluorine is unavailable, but its initial leachate value would place it in line with this cluster, suggesting the existence of fluorophosphates.

Much of the foregoing is speculative, but we also think that it is quite plausible. This discourse points out that generalizations can be made about the leaching behaviors of coal preparation wastes. Every coal waste situation is not unique, and the variables are not limitless. Acidity appears most important; both the ability of a waste to produce acid and its ability to neutralize the acid are critical. And last, a coal preparation waste is not bad just because it is a high-sulfur one.

D. Assessing the Pollution Potential

Quantitative knowledge about the existence and extent of the polluting capabilities of a waste is needed to evaluate whether control measures are needed. Once need has been established, this knowledge is also needed to define the types, magnitudes, and efficiencies of the control techniques that must be used to remedy the problems. Such information has been gathered for the trace elements of concern for coal preparation wastes in the Illinois Basin. Of the 69 elements studied, 12 were found to be released from these wastes in potentially hazardous quantities (E. M. Wewerka, J. M. Williams, and P. Wagner, "The Use of Multimedia Environmental Goals to Evaluate Potentially Hazardous Trace Elements in the Drainage from High-Sulfur Coal Preparation Wastes," in preparation). Preliminary assessment results for the low-sulfur Appalachian coal waste were reported in the third annual report of this project (LA-7831-PR). A more complete evaluation of the pollution potential of these wastes is reported here.

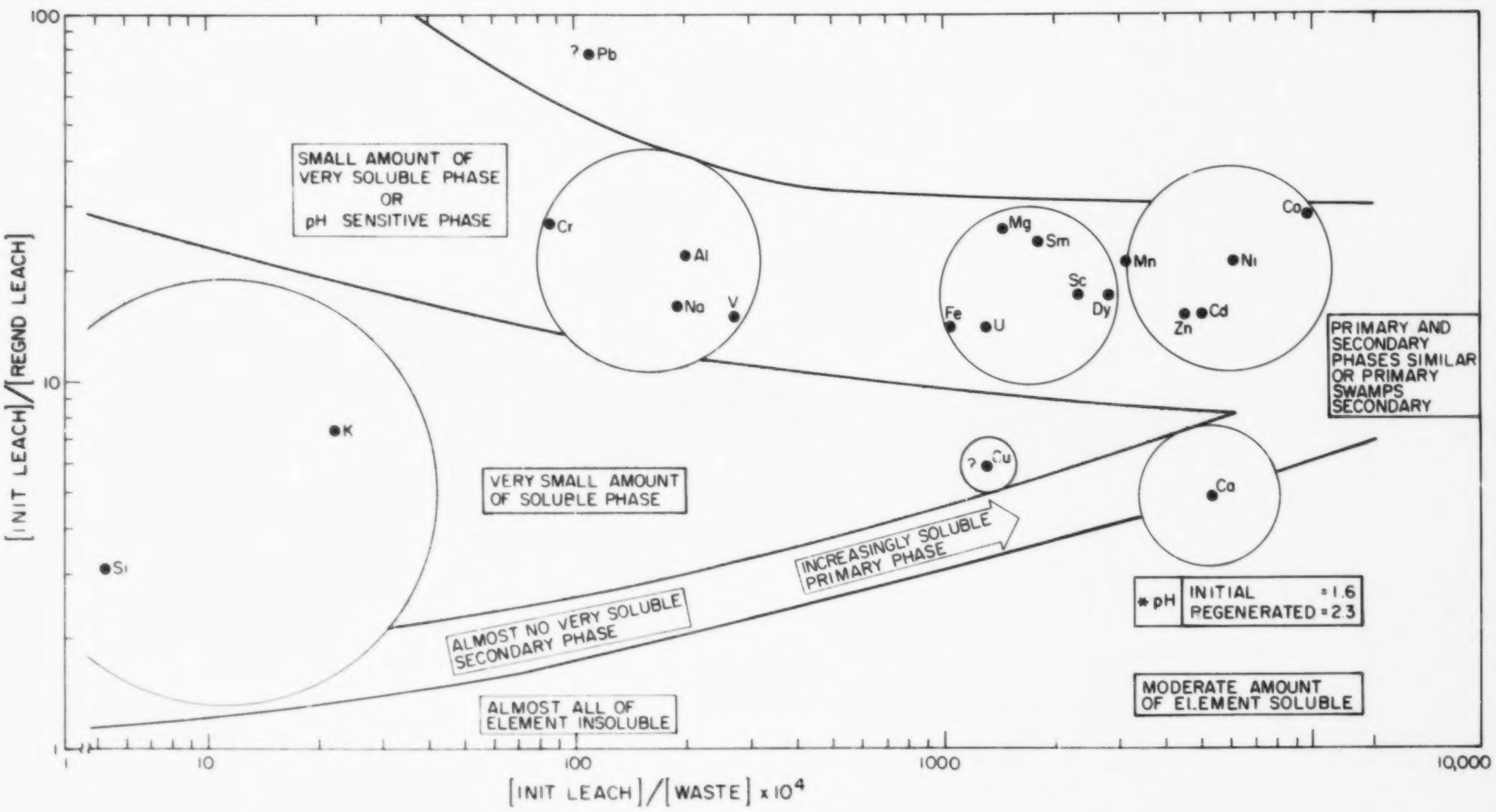

Fig. 27.
Elemental associations from the column leaching data of a high-sulfur coal waste.

Both batch and column leaching experiments can be used to evaluate pollution potential. Because they are thought to represent the real world better, column leachates have been favored and used in the past. The problem has been which ratio of liquid to waste should be used. For practical purposes, we have chosen the 100-mℓ increment taken after 400 mℓ of water have passed through 1 kg of waste. These leachates seem to correspond reasonably well with field samples (E. M. Wewerka, J. M. Williams, and P. Wagner, "The Use of Multimedia Environmental Goals to Evaluate Potentially Hazardous Trace Elements in the Drainage from High-Sulfur Coal Preparation Wastes," in preparation). For comparison we have chosen the 1-day-batch leachings in which the leachate-to-waste ratio is 5:1, but whose element-release data are reported in micrograms of element released per gram of waste leached. The EPA MEG/MATE system has been used to evaluate the element toxicity. Ecology MATE values have been chosen as representative of the most critical toxicity (see Task III on Bioassay). A dilution factor of 100 has been applied to all the leachate levels to simulate environmental dilution. Hazard factors reflect the ratio of the adjusted leachate level to the toxicity level (MATE). Values approaching or exceeding 1 are cause for concern. Hazard factors for 11 elements in column and batch leachates for wastes from the low-sulfur Appalachian plant and the three Illinois Basin plants are reported in Appendixes I and J, and are plotted in Figs. 28 and 29 as functions of the leachate pH. The most remarkable feature of these plots is the consistency in the behavior of the elements, regardless of their origin. Thus, elements that are hazardous in one waste are generally hazardous in another. Almost all elements also show a decrease in "hazardousness" as pH increases. Manganese, calcium, and potassium are notable exceptions. Aluminum and iron exhibit the strongest response to pH changes. These two elements are the most toxic in coal wastes that generate low pH values (< 2) but are also two of the least worrisome for wastes producing little acidity (pH > 6). Manganese and nickel are the only consistently worrisome elements.

Rating the elements in terms of their environmental impact and waste association is a tricky business. Indeed, our choice of the column leachates to test and our assumption of a 100-fold environmental dilution factor introduce about a 1000-fold reduction in the element levels that can be released. Without this reduction, most of the 69 elements that we have studied would be hazardous in one coal waste or another. Fortunately, the "hazardousness" ordering of the elements remains relatively constant. Thus, if a waste does not have the big offenders, it does not have the little ones either.

Based on our observation that the elements released by a coal waste are related to the acid-generating tendency of that waste, we have rated 69 elements with respect to their pollution potential. The ratings for high-sulfur Illinois Basin and low-sulfur Appalachian coal wastes are given in Table XIX. We believe that this evaluation has general applicability to all neutral and acid-generating coal wastes. Further work is needed to verify this opinion.

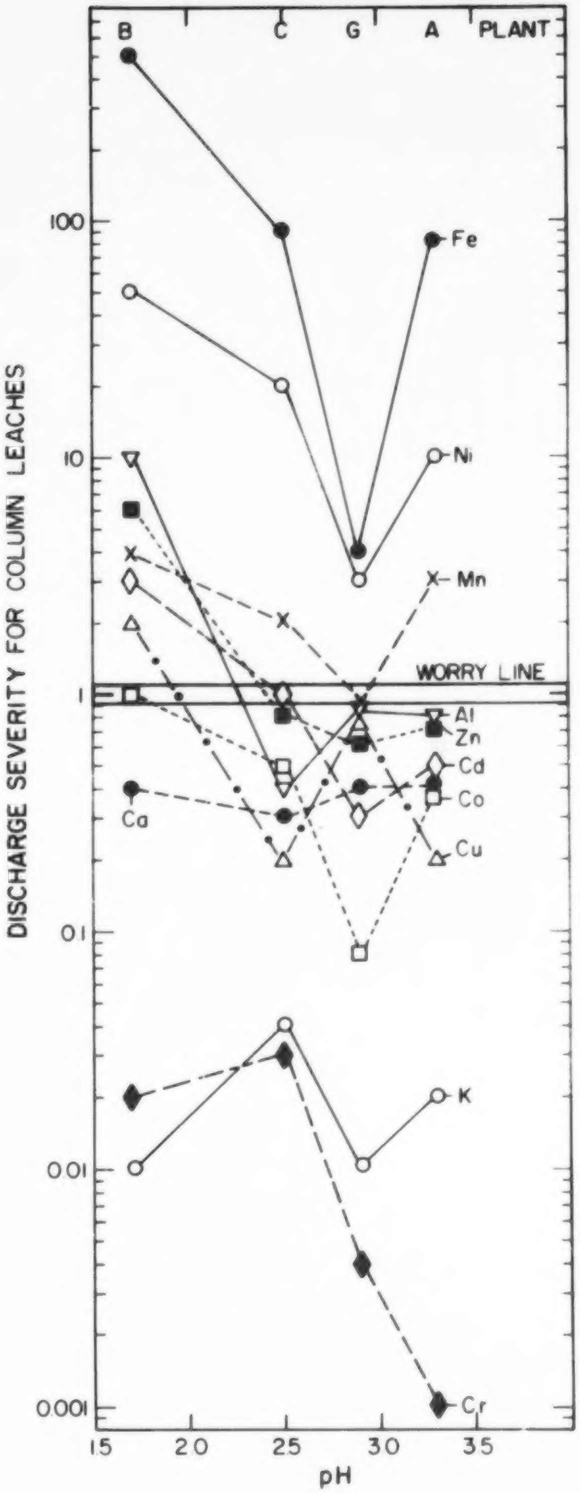

Fig. 28.
Discharge severity for column leachates of several coal wastes. (Values at 2:5 leachate:waste and reduced 100-fold.)

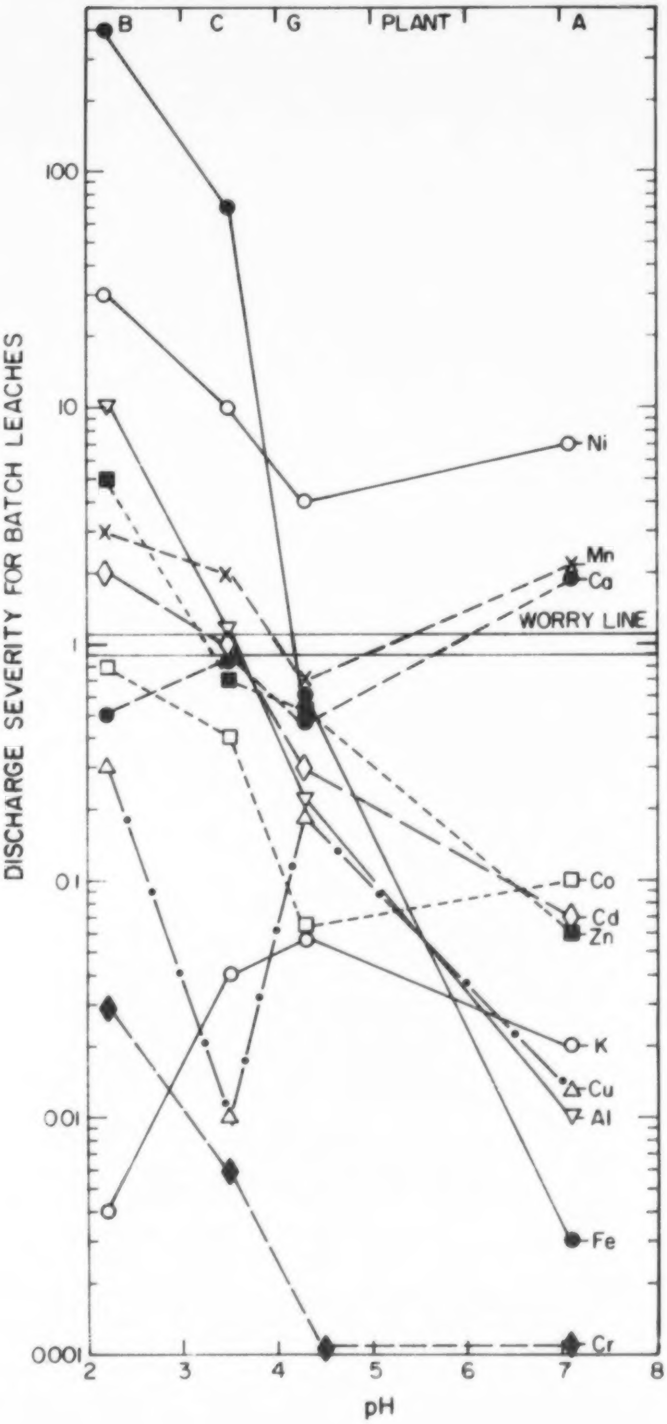

Fig. 29.
Discharge severity for batch leachates of several coal wastes. (Values in g-released/g-waste and reduced 100-fold.)

TABLE XIX

A RATING OF THE TRACE ELEMENTS OF CONCERN IN APPALACHIAN LOW-SULFUR AND ILLINOIS BASIN HIGH-SULFUR COAL PREPARATION WASTES[a]

Elements (2) of concern under acid *or* neutral conditions:
Ni, Mn

Elements (4) of concern under acidic (pH<4) conditions:
Al, Cd, Fe, Zn

Elements (6) of concern only under highly acidic (pH<2.5) conditions:
As, Be, Co, Cu, Pb, Se

Elements (36) not particularly hazardous under acid or neutral conditions:
Ag, B, Ba, Bi, Ca, Ce, Cr, Cs, Dy, F, Ga, Ge, Hf,
K, La, Li, Mg, Mo, Na, Nb, Pr, Rb, Rh, Sb, Sc, Sm,
Sr, Ta, Te, Th, Ti, Tl, U, V, Y, Zr

Elements (21) with neither an ecology nor a health MATE value listed. (All except S and P, occur at very low levels and are unlikely to be hazardous)[b]:
Au, Br, Er, Eu, Gd, Ho, I, Ir, Lu, Nd, Os, P, Pd, Pt, Ru, S, Sn, Tb, Tm, W, Yb

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[a] Based on EPA health and ecology MATEs and column leachates.

[b] Sulfur would probably fall under the 'highly acidic' category, while P would probably not be particularly hazardous even then.

III. TASK III: LEVEL I BIOASSAY OF (HIGH-SULFUR) COAL CLEANING WASTES AND WASTE LEACHATES

Toxicological characterizations of high-sulfur Illinois Basin coal waste leachates were performed on leachates that had been diluted 100-fold. Under these conditions 12 elements were shown to be of potential environmental concern. The samples chosen for study were Illinois Basin Plant C average solid waste (#18A) and its shaker-formed leachate. The chemical analyses for the waste are reported in our second annual report (LA-7360-PR), and an abbreviated list of elements and their concentrations for the leachate is reported in Appendix K under the "FRESHWATER ALGAE" heading.

A. Health Effects

The tests chosen to evaluate the damage the coal waste leachates could cause to higher animals and humans were listed in the document EPA-600/7-77-043 [K. M. Duke, M. E. Davis, and A. J. Dennis, "IERL-RTP Procedures Manual: Level I Environmental Assessment, Biological Test for Pilot Plants" (April 1977)]. The specific sections used were 3.3.1 (Mutagenesis or AMES test), 3.3.2.1 (Rabbit Alveolar Macrophage or RAM), 3.3.2.2 (Human Lung Fibroblast or WI-38), 3.3.2.3 (Clonal Toxicity or CHO), and 3.3.3 (Quantal Rodent Toxicity). Each of these tests was run at LASL by personnel in our Life Sciences Division (LS Division). Their results and observations are included in Appendix K. A quantitative summary of their findings is given in Table XX.

The Quantal Rodent Toxicity and AMES tests were negative for both leachate and solid waste. In the Quantal test, this means that the leachate can be ingested (drunk) undiluted in moderate quantities (corresponding to 700 mℓ for a 150-lb human) without short-term problems. In the mutagenesis test, this means that each of the four Salmonella strains tested produces as many revertants with the waste component present as without the waste component. A revertant is a genetic reversal of a mutant back to its normal form, as measured by a change in ability of the strain to metabolize certain nutrients.

The cytotoxicity (RAM, WI-38 and CHO) tests demonstrated that the waste materials can cause health degradation on the cellular level. The test sensitivity was CHO>RAM>WI-38, with only a factor-of-4 spread from CHO to WI-38 for the leachate. The more sensitive CHO test shows that the leachate is still toxic (50 percent reduction in activity) when diluted 1 part to 32. When this diluted solution is evaluated in terms of the constituent health MATE values (see Table XXI), Fe, Mn, and Ni are the only elements with potentially hazardous levels. At this level only iron, with a hazard factor of 11, would be singled out. Iron, apparently the trace element of primary concern, appears to be tolerable from a health standpoint at levels (15 ppm) above that set by EPA (3.5 ppm) for waste effluents.

The solid sample causes more (60 - 300x) degradation than the liquid samples in the cytotoxicity tests. Little of this difference seems to be related to the trace element content that the solid would release. We do not have a satisfactory explanation for this.

TABLE XX

QUANTITATIVE SUMMARY OF HEALTH EFFECTS TESTS FOR A COAL WASTE AND ITS LEACHATE[a]

Test	Test #	LC_{50}, LD_{50}, or EC_{50} (%)[b]			
		20 hour[c]	24 hour[c]	40 hour[c]	48 hour[c]
Mutagenesis (AMES)	3.3.1				
Leachate		Negative			
Solid Waste		Negative			
Rabbit Alveolar Macrophage (RAM)	3.3.2.1				
Leachate		7.5			
Human Lung Fibroblast (WI-38)	3.3.2.2				
Leachate				11	
Solid Waste				0.18	
Clonal Toxicity (CHO)	3.3.2.3				
Leachate (1 day)[d]			4.5		3.1
Leachate (1 week)[d]			4.5		4.5
Solid Waste (1 day)[d]			0.0125		0.0125
Solid Waste (1 week)[d]			>0.1		>0.1
Quantal Rodent Toxicity	3.3.3				
Leachate		>10mℓ/kg			
Solid Waste		>10g/kg			

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[a] LEACHATE is CTWT-1012: Iron concentration is 5460 ppm: SOLID WASTE is Plant C waste #18A.

[b] LC_{50}: Concentration of test material which causes mortality in 50% of test organisms.

LD_{50}: Dose of test material administered which causes mortality in 50% of test organisms.

EC_{50}: Concentration of test material which causes immobility in 50% of test organisms.

[c] Hours after inoculation.

[d] Colony growth time before inoculation.

TABLE XXI

TRACE ELEMENT CONCENTRATIONS AND DISCHARGE SEVERITY FOR LEACHATES GIVING EC_{50} [a]IN CLONAL TOXICITY TEST[b]

Element	Concentration (ppm)	Mate (ppm)	Discharge Severity
Fe	170	1.5	113
Mn	0.50	0.25	2
Ni	0.38	0.23	1.6
Co	0.18	0.75	0.2
Al	17	80	0.2
Cd	0.01	0.05	0.2
F	3.4	38	0.09
Ca	17	240	0.07
Cr	0.016	0.25	0.06
Zn	0.75	25	0.03
Na	19	800	0.02
Cu	0.05	5	0.01
		Total	118

[a] EC_{50}: Concentration of test material which causes immobility in 50% of test organisms.

[b] Leachate CTWT-1012 diluted 1 part to 32.

B. Ecological Effects

The tests chosen to evaluate whether the coal waste materials could degrade the ecological systems were those under section 3.4 of EPA-600/7-77-043. The specific tests were 3.4.1 (freshwater algae) and 3.4.2 (both fathead minnows and *Daphnia magna*). The algae tests were run at LASL in the LS Division, and the minnow and *Daphnia* tests were run by the LFE Environmental Analysis Laboratories of Richmond, California. The results are reported in Appendix K. Only leachate was tested. A summary of the levels at which 50% immobility or death occurs is given in Table XXII.

Algae and small aquatic life are sensitive to coal waste leachate. In general, these systems are a factor of 10 more sensitive than the health-related systems discussed above. (This difference is well-known and reflected by the MATE values EPA has given to many elements; e.g., Fe has a health MATE of 2.5 and an ecology MATE of 0.25; Mn, on the other hand, has values of 0.25 and 0.1, respectively, while Al has values of 80 and 1.) The lower limit for the algal test was not established and thus cannot be related directly to the values for the fishes. Of the two aquatic animals, however, *Daphnia magna* is several times more sensitive.

A quantitative assessment of the trace metal concentrations which give these results can be made with EPA ecology MATE values. Using the concentration for TLM_{96} (total lethal median, or that concentration of test solution in which 50% of the test animals die or, in the case of *Daphnia*, are inactive within 96 h of being exposed to the test solution) for the more sensitive *Daphnia magna*, hazard factors above 1 are found for only iron and nickel (see Table XXIII). At a safe concentration,

TABLE XXII

QUANTITATIVE SUMMARY OF ECOLOGICAL EFFECTS TESTS FOR A COAL WASTE AND ITS LEACHATE[a]

Test	EPA Test #	TLM_{50}[b] or EC_{50}[c] for Leachate (%)[d]
Freshwater Algae	3.4.1	<0.75
Fathead Minnows	3.4.2	0.45
Daphnia magna	3.4.2	0.17

---

[a] Leachate CTWT-1012 used.

[b] TLM_{50}: Total lethal median, concentration of test material which causes mortality in 50% of test organisms within defined test period.

[c] EC_{50}: Concentration of test material which causes immobility in 50% of test organisms.

[d] For example, 0.75% CTWT-1012 in test media.

TABLE XXIII

TRACE ELEMENT CONCENTRATIONS AND DISCHARGE SEVERITY FOR LEACHATES[a] GIVING TLM_{50}[b] IN *Daphnia magna* TOXICITY TEST

Element	Concentration (ppm)	MATE (ppm)	Discharge Severity
Fe	8.7	0.25	35
Ni	0.02	0.01	2
Al	0.88	1	0.88
Cu	0.026	0.05	0.52
Cd	0.0005	0.001	0.5
Zn	0.038	0.1	0.38
Mn	0.026	0.1	0.26
Ca	0.86	16	0.05
Co	0.009	0.25	0.04
Cr	0.001	0.25	0.003
K	0.027	23	0.001
		Total Hazard	39

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[a] Leachate CTWT-1012 dilution 1620 parts to 1 million.

[b] TLM_{96}: Total lethal median; concentration of test material which causes mortality of 50% of test organisms after 96 hours exposure to test material.

1/10th as strong as this, iron would still be above 1 at 3.5, suggesting that the MATE value for Fe may be a little low but again certainly not by much. Ruling out pH effects [the controls and test units were near the same values (6.2 - 6.7)], iron seems to be the main problem in the leachate.

C. Summary

Coal preparation wastes and their leachates are toxic but not excessively so under acute testing conditions. A qualitative evaluation of the Level I Bioassay tests is given in Table XXIV. Ecological systems represented by fathead minnows and Daphnia magna are an order of magnitude more sensitive than the most sensitive health system (CHO). The ecological systems test an organism's ability to survive when completely surrounded by the pollutant. The health systems measure the degradation of higher order, more diverse systems by a pollutant. In the most highly developed animals (rodents), coal preparation waste leachate was not found to be acutely toxic. Long-term or chronic toxicity is not known.

The high acidity (low pH) of the leachates was found to be toxic, but even when the acidity was neutralized, the leachates remained toxic. The active trace elements have been identified by EPA MATE values to be iron (Fe), nickel (Ni), and manganese (Mn), in that order. The original leachate contained 5500-ppm iron and needed to be diluted 1 part to 600 just to reach a concentration where 50 percent of the Dapnia magna could survive. A 1-to-6000 dilution, giving 1 ppm of iron, was acceptable for the most sensitive bioassay test run. From our study, future Level I bioassay testing of coal and coal waste leachates can be limited to the more sensitive ecological tests (fathead minnows and Daphnia magna).

TABLE XXIV

QUALITATIVE RESULTS OF LEVEL I BIOASSAY OF REFUSE AND REFUSE LEACHATES

Test	Solid	Leachate
Quantal Rodent Toxicity	Neg	Neg
Mutagenicity (Ames)	Neg	Neg
Cytotoxicity		
Rabbit Alveolar Macrophage (RAM)	Pos	Pos
Human Lung Fibroblast (WI-38)	Pos	Pos
Clonal Toxicity (CHO)	Pos	Pos
Freshwater Algae		Pos
Freshwater Fish (Fathead Minnows)		Pos
Daphnia		Pos

MISCELLANEOUS

I. WASTE COLLECTION SUMMARY

Since the project's inception, samples have been collected from coal preparation plants as the need evolved. A brief log of samplings is presented in Table XXV. Samples collected from plants for more extensive studies are in the 1500- to 2000-lb range. The 300-lb sampling of Plant D was exploratory. Generally the volumes of feed coal, clean coal, and waste have been comparable. The samples were usually collected from moving belts, although one waste sample had to be collected from a waste pile as the waste was being dumped, and a product-coal sample was collected from a just filled rail car. Shovelfuls were normally taken every 10 - 15 min. Plastic-lined, 10- to 12-gal. cardboard barrels were filled every 1 - 2 h. These were sealed and transported by truck or air back to the laboratory, where they were prepared further (see first and second annual reports, LA-6835-PR and LA-7360-PR). Some oxidation problems have been encountered. Sealing under nitrogen and storage at 4°C might have been helpful but were not tried. Plants A, B, C, and D were described in the first annual report. Information about Plants G, I, and K is given in Tables XXVI to XXVIII.

TABLE XXV

RECORD OF COAL-PREPARATION PLANT SAMPLINGS

	Plant										
	A	B	C	E	M	N	H	G	I	K	D
Location	Illinois Basin						Homer City	Appalachian			Western
Sulfur Level	High	High	High	High	High	High	High	Low	High	High	Low
Date Sampled	11/75	11/75	11/75	6/76	10/78	4/78	X	6/76	5/79	5/79	11/75
Total Weight (lbs)	2000	2000	2000	2000	30 000	(500 gal)		2000	1500	1500	300
Feed Coal	X	X	X	X				X	X	X	X
Coal Waste	X	X	X	X	X			X	X	X	X
Coal Waste Drainage						X					
Product Coal	X	X	X	X				X	X	X	

A large waste sample was collected from Plant M at the end of 1978 to provide a source for scaled-up disposal testing. This sample was scooped up by a front-end loader as it was dumped, fresh out of the plant, and poured into 55-gal. drums. Air-tight lids were then placed on the drums. Because of the nature of the ultimate use of this sample, no liners were used in the barrels. The drums were placed on a truck and shipped back to the laboratory for testing. Information about Plant M is given in Table XXIX.

A large sample of high-sulfur, acid mine, coal waste drainage was also secured for control technology studies. This sample was collected in 55-gal., plastic-lined drums and shipped by truck to the laboratory. This sample had little ferrous content, as oxidation had been extensive,

TABLE XXVI

INFORMATION ON PREPARATION PLANT G

Date Sampled	6/21/79	
Location	Eastern Kentucky	
Coal Seams	Coalburg and Stockton	
Cleaning Equipment	[illegible] x 6 in. rotary breaker 1/4 x 6 in. to heavy density media ([illegible] feed) [illegible] x 1/4 in. to Deister tables ([illegible] feed)	
Feed Rate	1000-1200 ton/h	
Product Coal	Whitish in appearance 0.88% Sulfur (company data) 10% Ash 12,200 Btu	
Sampled	Raw coal after crushing	3 x 13 gal
	Cleaned and dried coal	2 x 13 gal
	Refuse (fine and coarse)	3 x 13 gal
Observations	Streams clear of yellow boy, but muddy	

TABLE XXVII

INFORMATION ON PREPARATION PLANT I

Date Sampled	8/1/79 for 4 hours	
Location	Western Pennsylvania	
Coal Seams	Purchased coal that is blended	[illegible]%
	Old piles and seconds	[illegible]%
	Deep mines Lower Kittanning	[illegible]%
	Strip mines Upper Kittanning	[illegible]%
	Lower Freeport	[illegible]%
Feed coal properties	Company data March, 1979	
	Moisture (%)	4.51
	Ash (%, dry)	11.06
	Sulfur (%, dry)	2.80
	Btu	12,500
	% Float	65
Cleaning Equipment	1 1/4 in. rotary breaker Cyclones 1/4 in. clean coal	
Feed Rate	500 ton/h	
Sampled	Raw coal before breaker	1 x 13 gal
	Cleaned and dried	1 x 13 gal
	Refuse and breaker reject	1 x 13 gal
Waste disposal	Conveyored; thin-layered in shallow valley; clay-lined with drainage ditches; effluent collected and treated with mine water at lime plant 500 x 1500 ft pile, 20 ft high Uncovered without evidence of intermittent cover	

TABLE XXVIII

INFORMATION ON PREPARATION PLANT K

Date Sampled	5/3/79 for 3 hours	
Location	Western Pennsylvania	
Coal Seams	Purchased coal that is blended Upper and lower Kittanning Upper and lower Freeport	
Cleaning Equipment	-5 in. crusher 1 cell, Jeffery jig -2 in. clean coal -3/8 in. bypass	
Feed Rate	150 ton/h	
Sampled	Raw coal (5 x 1/8) Raw coal "clean" coal (1/8 x 0) Clean coal (2 x 1/8) Refuse (5 x 0) 60/40 fine/coarse split	4 x 13 gal 2 x 13 gal 4 x 13 gal 3 x 13 gal
Observations	pH adjusted in washing water with soda ash	
Waste Disposal	Trucked back to strip mine	

TABLE XXIX

INFORMATION ON PREPARATION PLANT M

Date Sampled	11/15/78 for 6 hours	
Location	Western Kentucky	
Coal Seams	Kentucky 9 and 11	
Cleaning Equipment	-6 in. crusher McNally jig	
Feed Rate	500 ton/h	
Sampled	Refuse (6 x 0) Steel drums sealed and shipped back to Los Alamos by truck	30 x 55 gal
Waste Disposal	Graded pile in elevated area. Waste dumped in 3 ft-high piles and spread in 6 in. layers. Pile uncovered.	

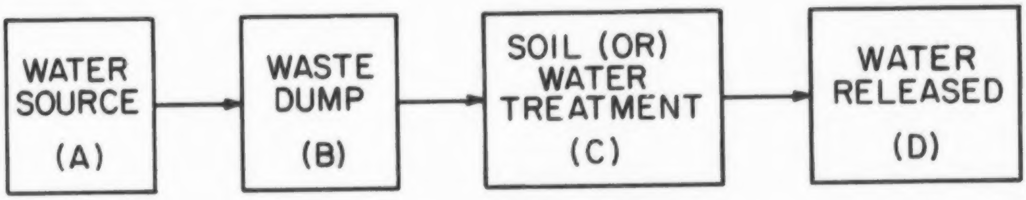
and was quite dilute, as it was collected in the spring during high water flow.

II. DEVELOPMENT OF ASSESSMENT METHODS

Control technology researches at LASL are being addressed in several areas related to energy production. As a consequence, we have been investigating a number of areas that have general significance to the ultimate understanding, measurement, and control of pollution from coal preparation waste. In the next few sections we present several of these multiprogrammatic efforts.

A. Batch Leaching, LASL, ASTM, EPA, and RCRA

A major problem in relating real life water pollution to laboratory simulations is deciding just what to simulate. The overall problem is depicted in the following diagram; the main concern was to release water that is environmentally safe. From a management point of view, however, knowledge of which parameters are responsible for the release and control of the pollutants is desired.



For several years we have conducted our own leaching tests in a manner now employed in the ASTM Method A leaching test. While we believe this gives a fair representation of the waste behavior, some questions have always remained: how important is the leaching medium in determining the trace element levels leached from a waste, and can we use this knowledge to build a better dump? To address these issues we have run several series of leaching tests. One set of tests studied the release of trace elements under a wide range of acidities using highly buffered extractants. This set included pH values from 1.4 to 9.7 and included a high-sulfur coal preparation waste; an eastern fly ash; and an Illinois, kaolinite-type soil. The experimental descriptions and results are given in Appendix L. A second set of tests studied the attenuation of trace metals already in solution by pH adjustments. The details of this set are reported in Appendix F and are discussed further in connection with waste effluent treatment under the Task I section.

Highly buffered leaching media of different acidities can give significantly different leachabilities for trace metals in solid materials. This is clearly illustrated by Figs. 30 and 31, where the amounts of iron leached from an eastern fly ash and an Illinois soil are shown to be sensitive to pH outside the range pH 5 to pH 8. In these two cases, the test needed little acetic acid to reach pH 5, and the leaching behavior was similar to that found for the water control. Using highly buffered acetic acid as described in the ASTM method B, however, gave greatly different results for the two materials. This behavior for acetic acid is very different from that of the phosphate and sulfate

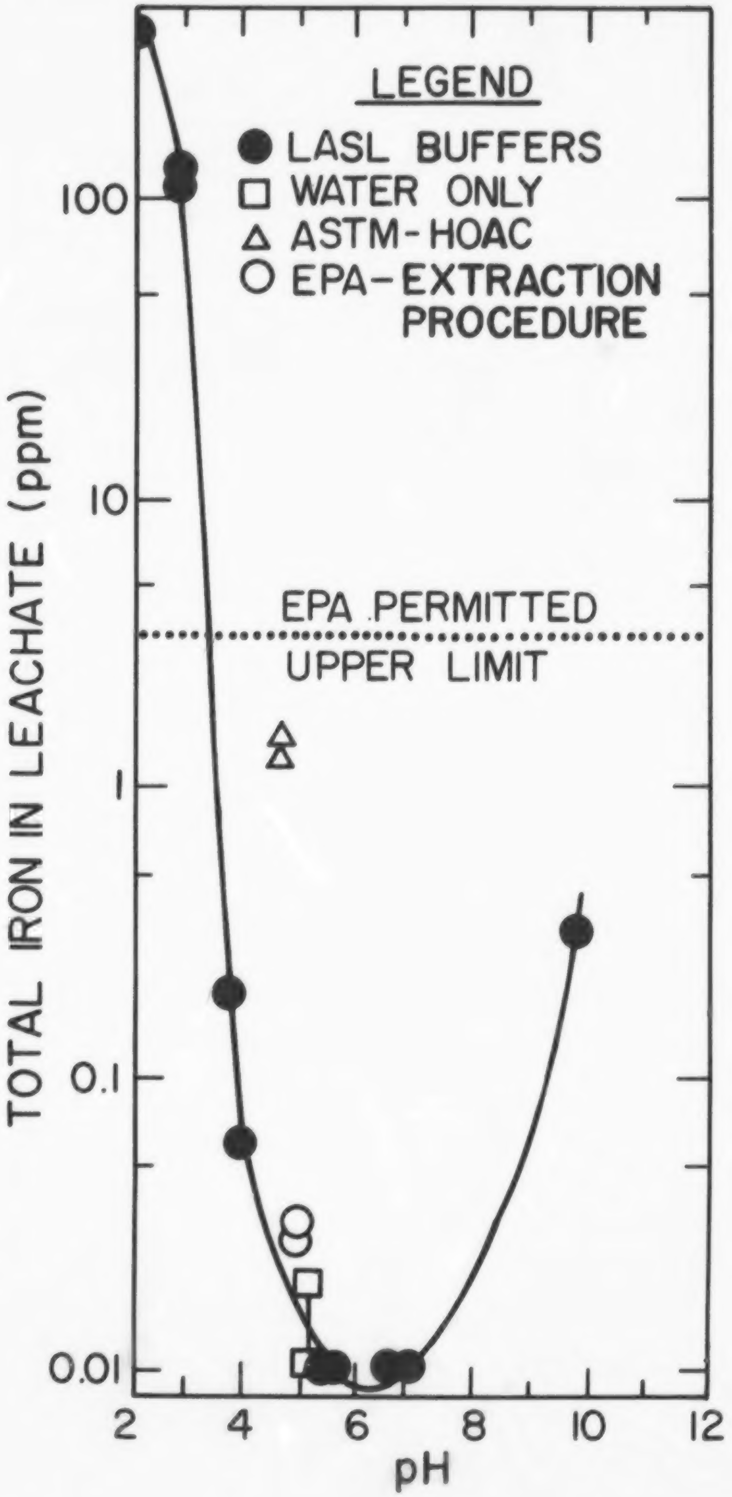


Fig. 30.
The pH influence on the leachability of iron from an eastern fly ash.

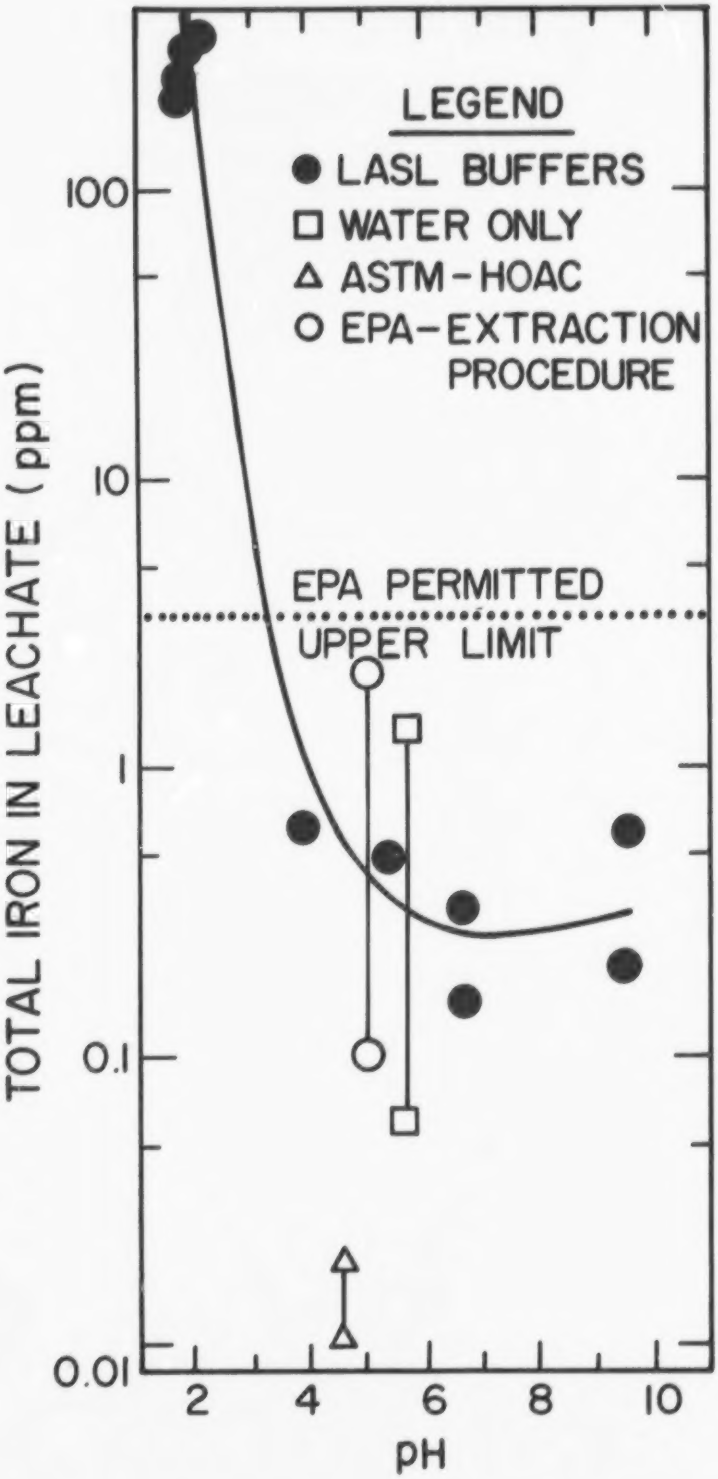


Fig. 31.
The pH influence on the leachability of iron from an Illinois soil.

buffers. Organic chelation might be important. At any rate, the acetic acid buffer gives a different picture, and cases where much acetic acid is needed to lower the pH should be viewed cautiously.

The concentrations of many trace elements drop as the pH of the leaching medium increases, and low values are achieved near pH 8. (This can be seen for the 13 trace elements leached from a high-sulfur coal waste in Appendix L, Table L-IV). At pH values much higher than 8, a few trace elements such as Mo are released at levels that could be cause for concern. From an environmental viewpoint, a dump should be kept around pH 8 to maintain the lowest overall release of trace metals.

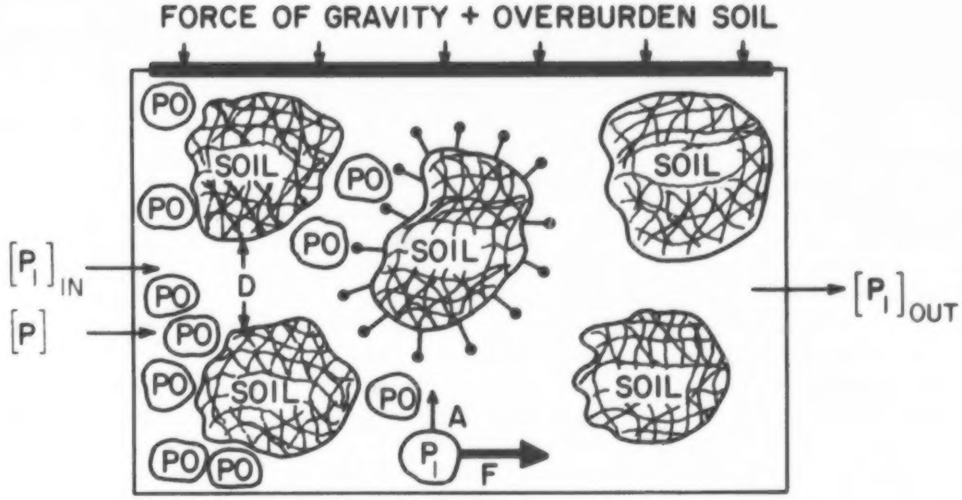
What is happening under the various leaching conditions is not completely understood. At low pH, the metals are certainly leached and remain in solution. At higher pH values, the metals may not be leached at all, or they may be leached and then reprecipitate. Thus, when the pH is raised on a coal waste leachate by adding lime, the metal concentrations behave in the same manner as the buffered leachates (compare Fig. 11 with Fig. L-1 for iron, and Table F-I with Table L-IV for some others).

Whether or not a metal is leached and reprecipitated or never leached at all may not seem significant, but the mechanism is important to a waste control technology designed to reestablish the previously existing environment. For example, iron and sulfur could be leached from pyrite and then redeposited as ferric oxide and calcium sulfate. When placed in a closed dump, the iron will be converted to the more soluble ferrous state as reducing conditions develop. If the sulfate is reduced to sulfide and the iron and sulfur have not migrated away, pyrite formation should occur in time. In any case considerable reorganization must occur to return these materials to their former state, namely pyrite. If, on the other hand, iron and sulfur are not oxidized and leached, they may already be in their most likely final states and extensive chemical reorganization will not be encountered as the pile reverts to its "original", reductive environment. These comments emphasize the importance of minimizing the weathering of natural wastes, such as coal waste, and rapidly returning the dump environment to the original geologic conditions.

B. Column (Dynamic) Leaching

The manner in which a leachate flows through a column can affect the levels of trace metals in the effluent. Chemical reactions are controlled not only by the interaction between two species, but also by the diffusion or transport rate of these species to and from the reaction site. Understanding transport phenomena is particularly important in evaluating data from studies of pollutant attenuation inside and outside waste dumps. A simple illustration of the flow problem is shown on the next page.

Leachate movement is determined by the difference between the inlet force and outlet force on the leachate and the size of the channels (D) between the soil (or waste) particles. These channels may be large cracks or fissures at one extreme and small capillaries, as illustrated in the soil particles, at the other. Water flow in the cracks will be fast; flow in the capillaries will be slow. The size of the channels will be determined, among other things, by the plasticity of the soil



particles and by the pressure exerted by gravity and the soil or overburden. For example, clays are deformable when wet and will generally compact, resulting in small channels and low flow rates.

Pollutant movement is determined by the flow of the leachate and the various available chemical reactions. Elements with very facile reactions available, such as those of ferric and aluminum cations with water at pH values above 4, should be less sensitive to leachate flow rates than those having only slower mechanisms available. Ferrous cations, for example, are not readily attenuated by "neutral" water and must find cation exchange sites on the soil particles to be attenuated. (See the section on "Pollutant Attenuation and Movement Through Soils" for possible Fe^{++}-Mn interactions in soils.) As the water flow slows, these reactions can be accomplished more easily.

Over the past 4 years, we have run a number of column experiments. For convenience we have used up-flow at 0.5 mℓ/min in 4.6-cm-diameter tubes. This seemed like a good compromise for the column leaching of coal waste. Recently, however, we noticed that, in soil attenuation experiments, rapid flow (1 to 5 mℓ/min) of leachate to prewet the soil gave little attenuation of some elements which had previously been attenuated in equilibrium studies. This increased our concern about conducting meaningful flow experiments. Consequently, as part of our efforts to evaluate the transport of trace elements through soils, we have begun to evaluate the influence of flow parameters on leaching results. Preliminary results for up-flow versus down-flow through several soils are presented here. Further experiments are planned and will be reported as they develop.

A simulated coal-waste leachate (see the section on "Standard Coal Waste Leachate") was diluted with distilled water to provide an influent leachate with a pH of 2.7, a Fe^{++} concentration around 450 µg/mℓ, and a Fe^{+++} concentration around 250 µg/mℓ. Glass columns (4.6-cm I.D. by 20-cm high) were packed with about 150 g of subsoil or overburden material to a bulk density of about 1 g/cm^3. Columns were evacuated and then slowly filled with leachate solution by allowing leachate to displace air in void spaces in the evacuated columns under gravity flow. A leachate pressure drop of 20 in. of water was maintained in the downward-flow columns. Flow rates for the gravity flows varied, depending on permeability of the packed columns. Flow rates of columns operating with upward-flow under pump control were between 1.2 and 5.0 mℓ/h, at constant head. Eluent was collected continuously, and periodic aliquots were taken for immediate determination of pH, Fe++ and total Fe.

The first soil used was Kentucky coal seam No. 11 overburden with a cation exchange capacity of 0.098 meq/g. Ferrous ion concentration in the effluent relative to the influent is given in Fig. 32. Down-flow resulted in more attenuation than up-flow. The first signs of Fe++ were 23% higher, and at $C/C_0 = 0.5$, the Fe++ was 18% higher. The Fe++ attenuated by the soil column with down-flow at $C/C_0 = 0.5$ was 0.096 meq/g of soil, in good agreement with cation exchange capacity of the soil.

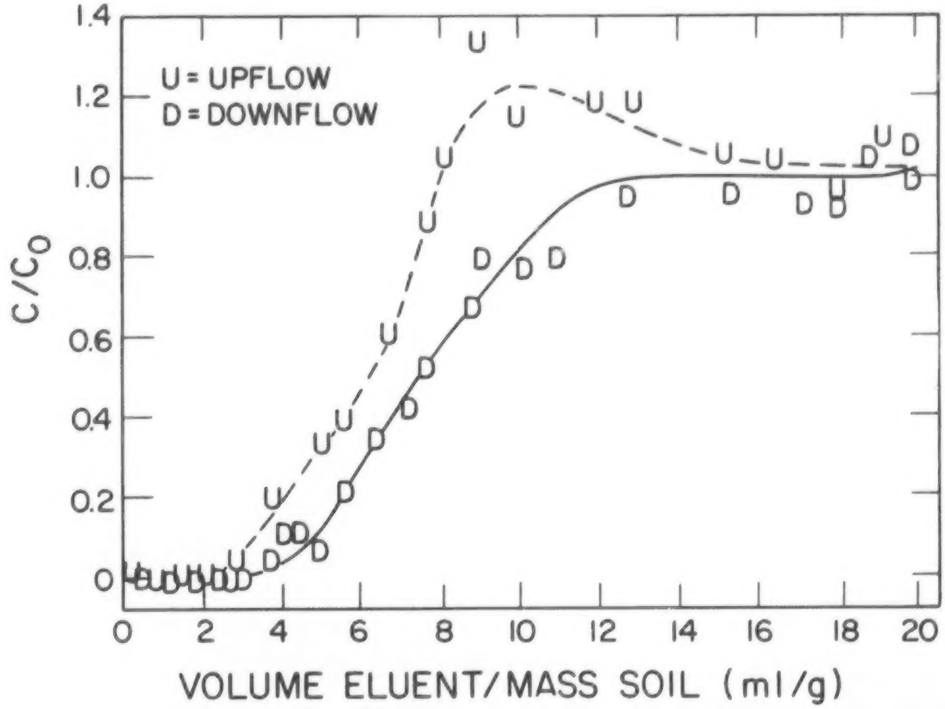


Fig. 32.
Ferrous ion attenuation by Kentucky coal seam No. 11 overburden as a function of the direction of leachate flow at comparable flow rates.

A second comparison using a glacial till subsoil from Illinois gave similar results. This soil was much more alkaline, but the first appearances of Fe++ occurred 13% earlier for up-flow than for down-flow. The flow sped up during breakthrough as was the case for the Kentucky coal seam.

In summarizing our current understanding of column attenuation, we would say that down-flow approaches equilibrium conditions better than up-flow, and that 1-mℓ/h flow is the maximum advisable for soil columns with a cross-sectional area around 15-20 cm^2. If up-flow is used, attenuation results are likely to be lower by 10 - 25%.

C. Visual Presentation of Statistical Results

For several years, we have presented our clustered data in graphical form. In addition to this black-and-white form, we have used a colored display for talks and for easier inspection. We believe this method of presenting the data is useful and have now made it available in a report. The report is available from NTIS or LASL as LASL document LA-7943-MS, entitled, "SORTNGO: A Program to Sort Matrices and Produce Graphics." This document presents a discussion of the method and lists the computer programs needed to carry out the operation.

D. Pollutant Attenuation and Movement Through Soils

As an adjunct to our studies on the ability of solid materials to attenuate trace elements (see the section on "Moderating the Disposal Site with Abaters"), we included efforts to evaluate the movement of trace elements through the solids. Although extensive, these efforts are still preliminary and only designed to pave the way for more sophisticated experiments. The methods used were 1) batch experiments in which more and more dilute solutions of an original leachate were equilibrated with different aliquots of soil (see Appendix E), 2) batch experiments in which leachate previously equilibrated with a soil was repeatedly equilibrated with new aliquots of soil (see Appendix D), and 3) column experiments in which leachate was passed through a soil and the effluent monitored (see Appendix M). Comments about the results of each will be followed by a brief, generalized discussion.

Approximating trace element transport through soils by equilibrating increasingly more dilute original leachate with aliquots of soil has several advantages, of which the ease of conducting the experiment is probably foremost. Large quantities of leachate can be used at each step. Atmospheric control is also possible, allowing oxygen-sensitive species, such as Fe^{++}, to be determined.* A major disadvantage of this method is its failure to account for previous attenuation, or lack of it. This is particularly critical when significant pH changes occur. The behavior of manganese (described below) is a good example. In spite of this problem, this method does give a quick assessment of how some elements are attenuated as leachate passes from one unit of soil to the next.

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*Columns do this well too, but batch methods which require repeated use of the same leachate give too many chances for error, especially when the pH changes to a range in which oxidation is very rapid (see the successive equilibration method).

Results for Al, Fe++ and Mn under this dilution-equilibrium method represent the major behavioral types and are given in Fig. 33. (Results and plots of these, plus As, F, Fe+++, and Ni, are given in Appendix E for 10 solids.) The solids used in Fig. 33 are noted in the legends: QLS is a quarry limestone; S-11 is a calcareous subsoil just above Kentucky coal seam No. 11; LOESS is a weathered, Illinois subsoil (OKAW); and TILL is an unweathered, calcareous, glacial till from Illinois. The C/C_0 values represent the amount of attenuation at each equilibration. Attenuating abilities of the soils were discussed in the section on "Moderating the Disposal Site with Abaters."

As the leachates became more dilute, the pH of the effluent rose. The final pH approximated that for the water-solid equilibrium (4.8 for LOESS and 7.5 - 7.9 for the others). This rise in pH was generally accompanied by a decrease in trace element content in the effluent (as illustrated by LOESS versus others for Al in Fig. 33 at a "solids-to-leachate" ratio of 0.5). Fe++ showed less pH-dependence (compare LOESS and TILL), but showed good attenuation as the leachate contacted more and more solid. Some ion exchange was likely, although some oxidation of Fe++ to Fe+++ may have occurred in spite of our efforts to prevent it. This behavior was typical of most of the ions (As, F, Fe+++, and Ni). Manganese behaved like Fe++ in the presence of the limestone tested (also in the presence of EC and ESP power plant ashes), but its behavior in the soils was dramatically different. In these, Mn was released in 5- to 30-fold greater quantities than were present in the influent. We think that the soils contained Mn which was somehow released by components in the leachate, since pure water released little Mn from the soils. If this continued release of Mn is due to acid neutralization by manganese-containing minerals, then batch leaching experiments in which previously equilibrated effluent is used could be conducted for the next equilibration to clarify the situation.

Conducting attenuation experiments by equilibrating previously attenuated leachate with new solid has the main advantage of incorporating differential attenuation. Thus pH-sensitive ions such as Al+++ and Fe+++ will generally be attenuated quickly and not enter too strongly into later equilibrations. Major disadvantages to this method are rapidly diminishing quantities of leachate, which limit analyses, and multiple handlings of the same leachate, which increase the chances for oxidation.

We have conducted a series of such attenuation experiments with 11 solid materials, using a 5100-ppm iron (mainly Fe++) leachate. Most of these solids were weathered and unweathered soils that covered a range of types (alluvial, glacial till, loess, and organic, plus some standard clays and limestone). A list of the materials, some of their properties, and the trace element levels for Al, As, Ca, Cd, Co, Cr, Cu, F, Fe, Mn, Ni, and Zn in the effluents are given in Appendix D. In addition to treatment with leachate, each solid was also leached with water and 0.14M sulfuric acid (equivalent to the total acidity of the leachate) to provide information about the ability of the solids to contribute trace elements and control pH. An evaluation of the ability of the sulfuric acid solution to reflect the pH effects on the solids is given by Fig. 34. Sulfuric acid tends to overstate this pH effect at low pH values. This would be due to the incomplete oxidation of the Fe++ in the coal-waste leachate, which accounts for much of the acidity in the coal-waste leachate.

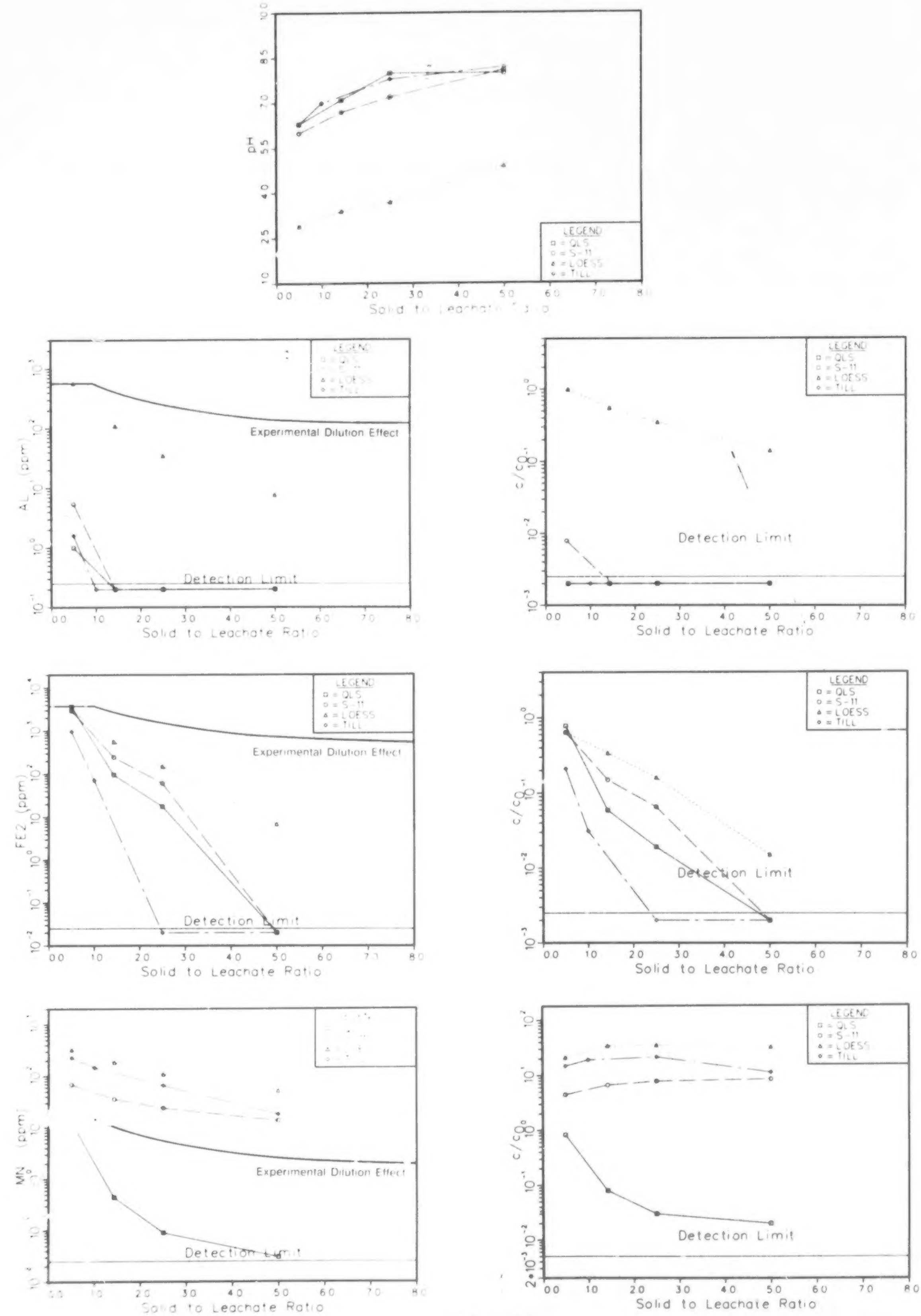

Fig. 33.

Trace element attenuation by increasing amounts of a soil acting on a coal waste leachate.

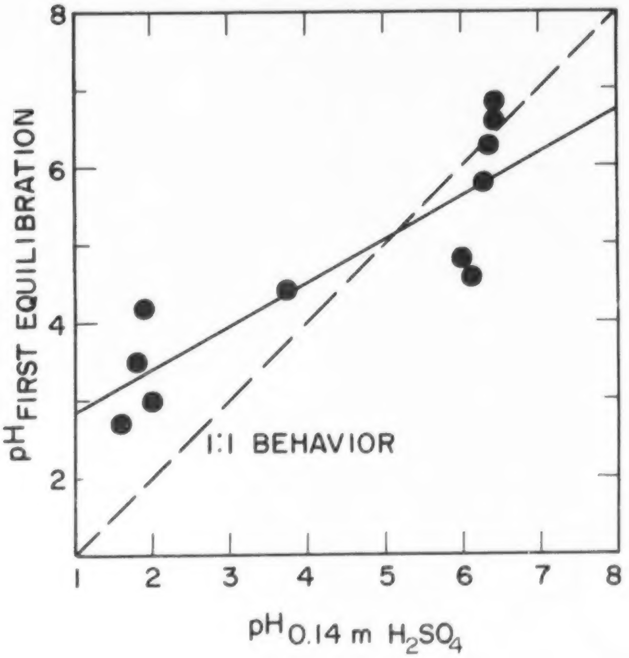

Fig. 34.
The pH of effluent from coal waste leachate-solid mixtures (2:1) as a function of the same solids in 2:1 mixtures with 0.14M H_2SO_4.

Major trace element behaviors are represented by the Fe and Mn results shown in Fig. 35. Most metals behaved like Fe and dropped rapidly as the leachate came in contact with more and more solid material. The effect appears to be mainly pH-related. If the pH was low (around 3), little attenuation was observed, even for Al. In the presence of non-soil solids, Mn also behaved this way, as illustrated by its attenuation by $CaCO_3$ in Fig. 35. When the coal-waste leachate interacted with the soils, copious quantities of Mn were released. In some cases, 400 - 500-ppm levels of Mn were found in the effluents! As the leachate passed through much larger amounts of soil, however, Mn did become attenuated. Calcium showed little tendency to be attenuated and normally showed a slightly higher level in the effluent than was present in the influent.

The behavior of Mn in the soils for the two types of batch attenuation experiments was similar and surprising. Obviously, Mn was being released by the soil, but how? Our first thought was that it was being released from a carbonate during the neutralization of the influent acid. Leaching the soils with sulfuric acid proved this not to be a major factor (see Fig. 35). Then we noticed that the level of Mn in the effluent was related to the influent level of Fe++ (see Fig. 36). It seemed likely that Fe++ was ion exchanging with Mn++, but observing that most of the really high Mn values occurred with weathered soils suggested that Mn release from amorphous MnO_2 might be important. Electrochemically this is possible.

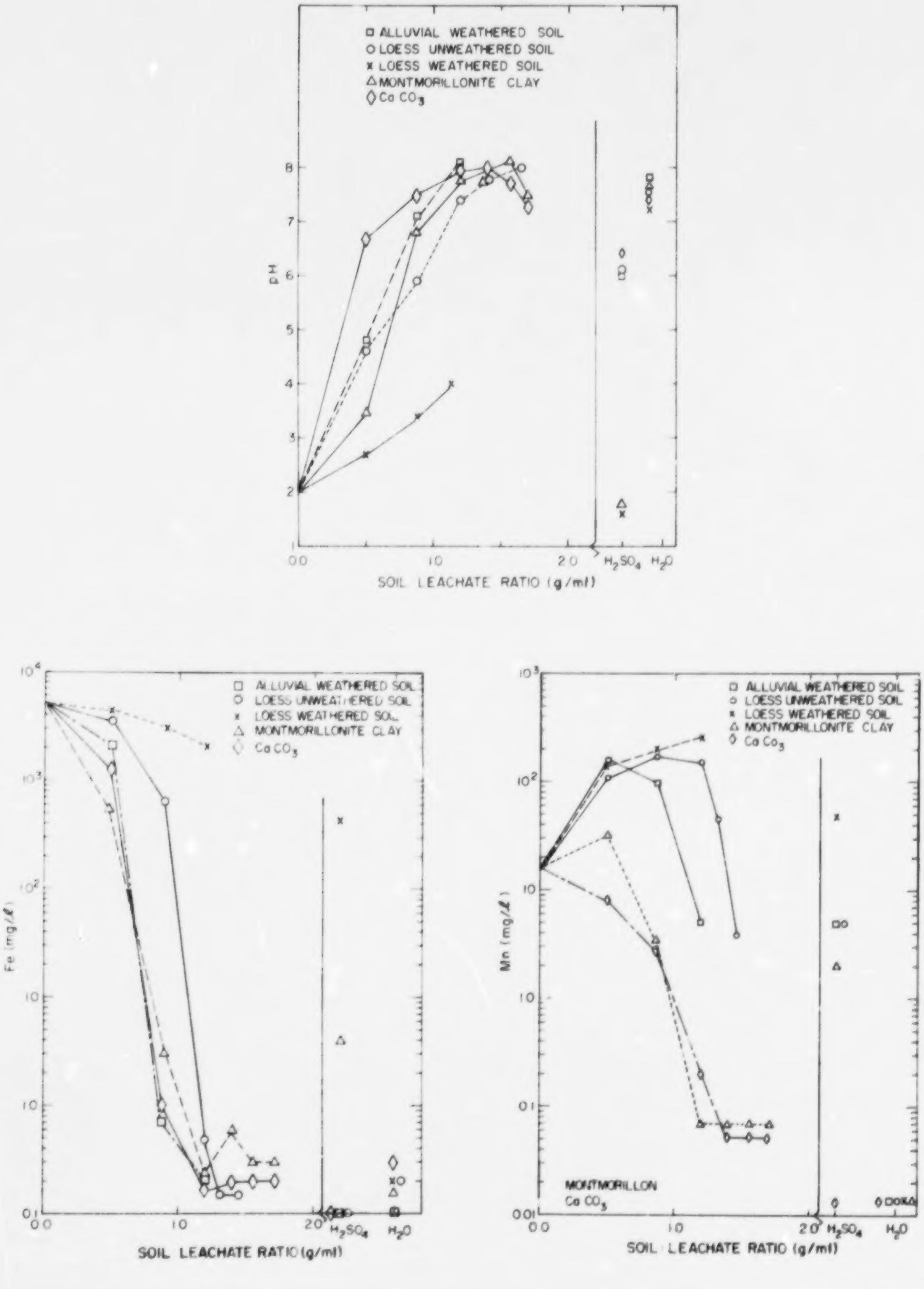

Fig. 35.
Trace element and pH levels of leachates from successive batch equilibrations with sorbents.

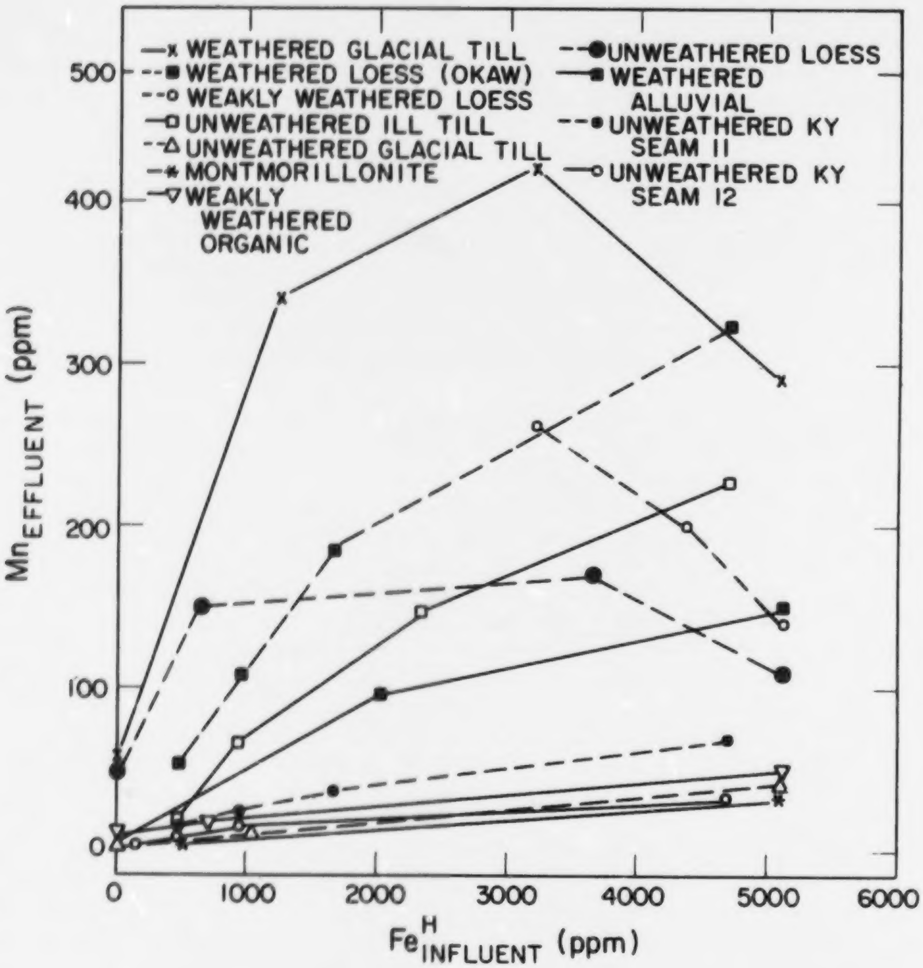

Fig. 36.
Manganese levels in effluents from soils treated with coal waste leachate as a function of influent Fe⁺⁺ levels.

$$MnO_2 + 2Fe^{++} + 4H^{+} \rightarrow Mn^{++} + Fe^{+++} + 2H_2O{:}E^{o} = 0.44\ V$$

Whatever the mechanisms, these results point out the need to understand complex interactions among trace element species and soils as well as individual, trace element-soil interactions.

Column attenuation experiments are thought to more closely resemble natural soil-leachate interaction. With minimal channeling and slow flow, they correspond to a multitude of batch equilibrations between minute amounts of soil and leachate. Channeling and fast flow could make column experiments less meaningful than batch experiments and could even prove detrimental by giving meaningless results (see the section on "Column (Dynamic) Leaching").

The experiments reported here are first efforts; they point out some parameters which can affect the execution of the experiment, and they give some information about the behavior of several trace elements. Columns were packed with fine-grained soils (an unweathered, calcareous till and a weathered loess soil). Concentrated, coal-waste leachate (4000 ppm Fe++) was passed slowly down through them. Trace element levels and pH values were monitored and are tabulated in Appendix M.

The results for the unweathered, calcareous till (Fig. 37) correspond well with those observed in the batch experiments for similar materials. As long as the pH was high, Al and Fe+++ were well attenuated, so well, in fact, that the column became plugged at a leachate:soil ratio of 6:1. Bivalent ions were attenuated but quickly broke through under the high influx. Ca passed through and Mn was released in small constant quantities by the soil.

The results for the weathered loess soil (Fig. 38) also agreed with the batch results but added several additional features. The pH was lower at all effluent volumes since there was less neutralizing agent present than in the till above. Initially, Al and Fe+++ precipitated in the soil. As the pH dropped, the deposited Al began to dissolve and move further through the soil, as did the soluble aluminum originally present in the soil. Added together these dissolved Al species formed a front (or wave) which slowly moved through the soil. Even the less pH-sensitive Fe++ and Ni++ ions showed this wave phenomenon. Column overload probably identified a phenomenon that might not easily surface otherwise. Ca was generally independent of the conditions. Mn, however, was released in large concentrations early and eventually decreased to levels approximating those of the influent. Some of the Fe++ attenuation may be related to this. (Recall the discussion about Mn release in the batch experiments above.)

The most apparent problem with this set of experiments is column overload. Because of this, the high soil-to-leachate ratio phenomena are obscured by the time that sufficient effluent has been collected. One remedy is the placement of a small quantity of concentrated leachate on the soil at the inlet and the use of distilled water to transport it as is common in chromatographic columns. Another is the use of a continuous stream of more dilute leachate. The latter is probably closer to real life. Using lower influx concentrations should permit ready evaluations of the amounts of soils needed to reduce the less pH-sensitive trace elements to acceptable levels.

Trace element transport through soils is variable and affected by many parameters. An experiment designed to evaluate these might be simple, but is more likely to include several perturbations. It is clear that complex interactions are occurring and that overloading the soil will quickly eliminate information about the ultimate ability of a soil to reduce pollutants to acceptable levels. Overloading may accentuate phenomena such as wave fronts, however. Simulating systems too simply may ignore or not identify some phenomena, such as that found for Mn in the experiments above. Batch equilibrium experiments do give results which can be related to column experiments. Redox conditions are important and eluent streams should be protected. In short, transport behavior can be measured, and soils do attenuate trace elements. Knowing

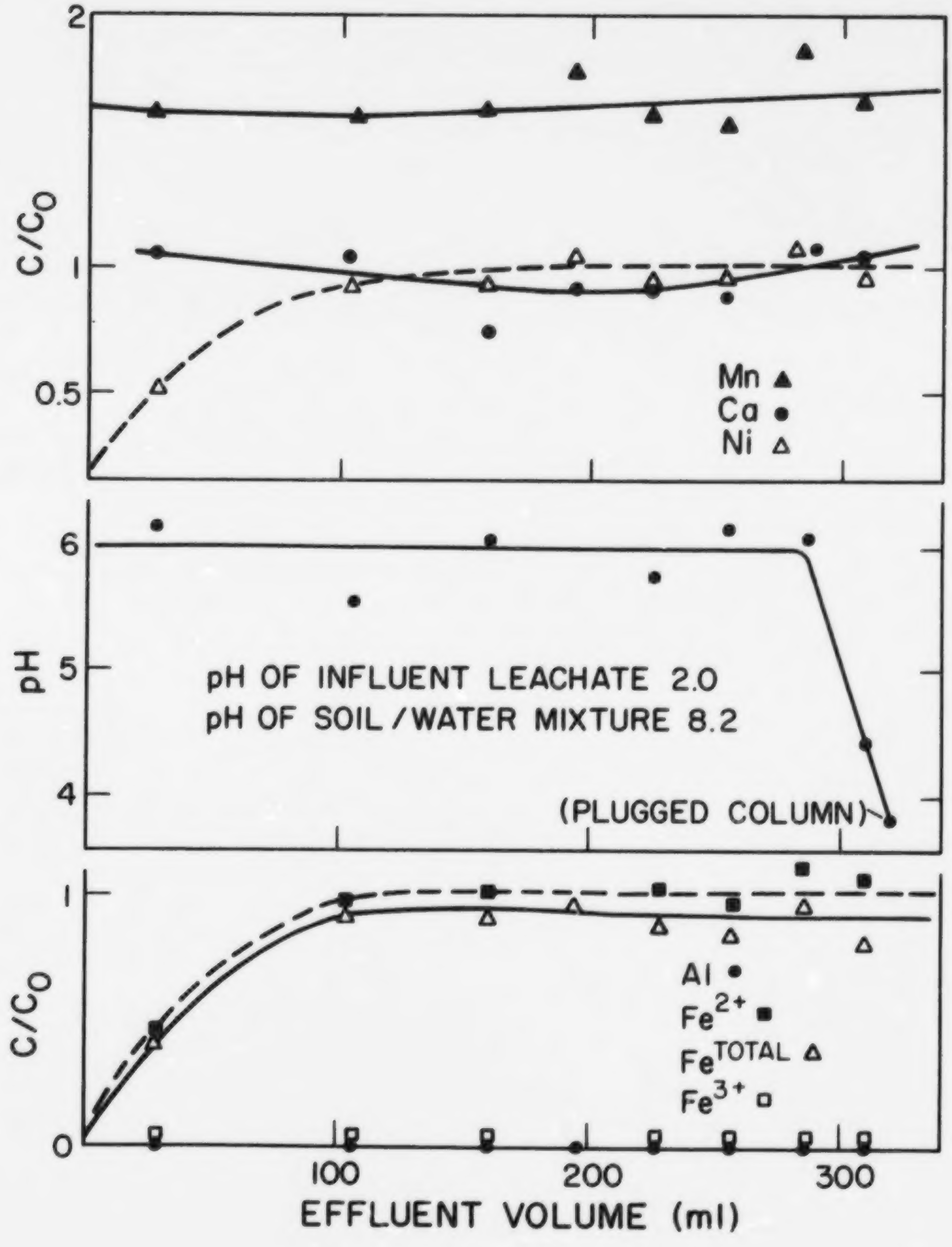

Fig. 37.
Trace element and pH levels of effluents from a column packed with an unweathered, calcareous till.

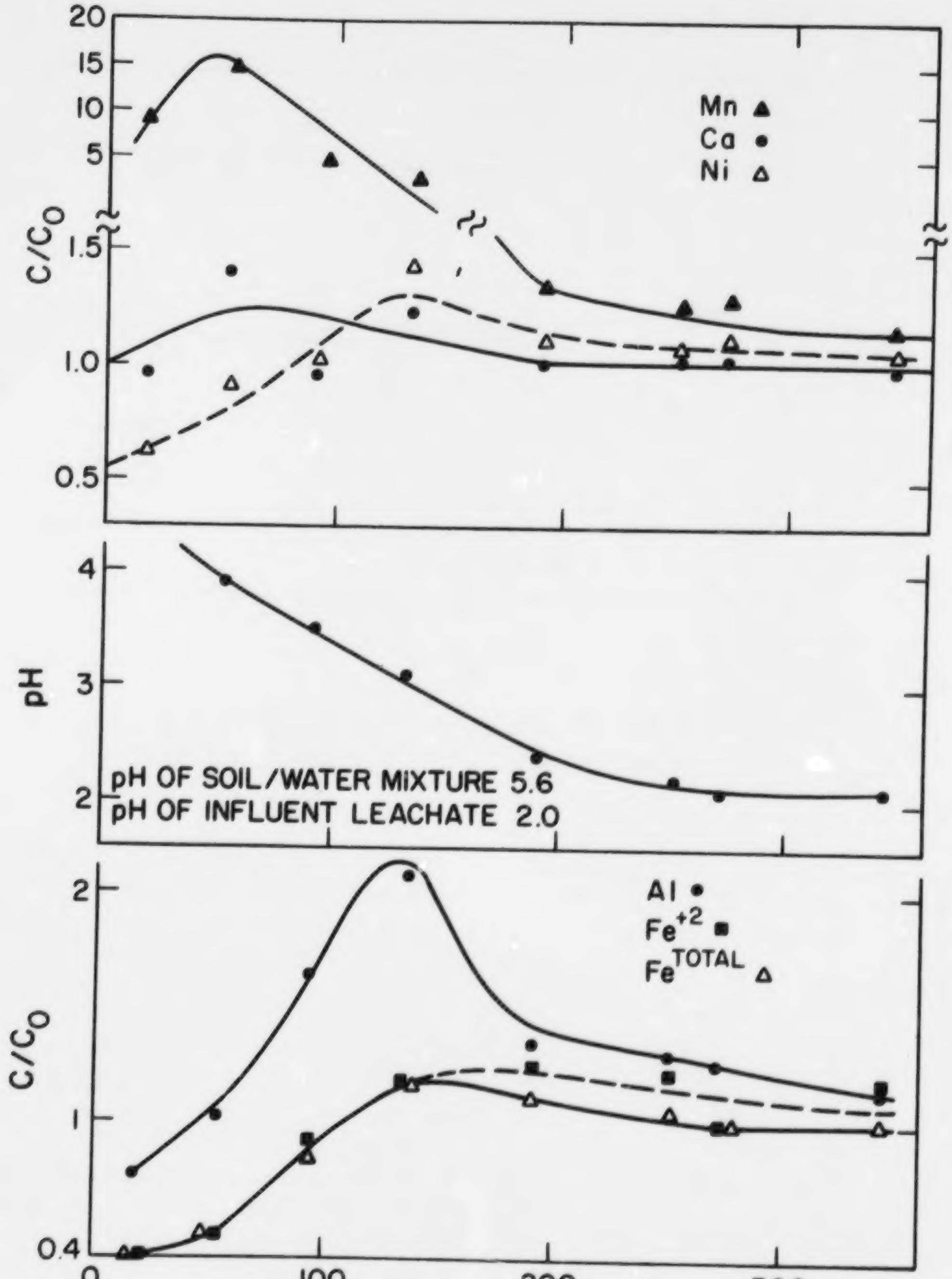

Fig. 38.
Trace element and pH levels of effluents from a column packed with a weathered loess soil.

how well and how fast could give a waste disposer valuable, maybe priceless, flexibility and allow him to operate when technical or economic restrictions were otherwise prohibitive.

E. Spark Source Mass Spectrometry (SSMS) Analyses

SSMS is an attractive technique for semiquantitative analysis of coal and coal-related solid and liquid samples for all elements [J. W. Hamersma, S. L. Reynolds, and R. F. Maldalona, "IERL-RTP Procedures Manual: Level I Environmental Assessment," EPA-600/2-78-160a (June 1976)]. In conjunction with the MEG/MATE system of analysis [J. G. Cleland and G. L. Kingston, "Multimedia Environmental Goals for Environmental Assessment," EPA-600/7-77-136a,b (November 1977)], an effective diagnostic is to locate sources of possible trace element contamination (E. M. Wewerka, J. M. Williams and P. Wagner, "The Use of Multimedia Environmental Goals to Evaluate Potentially Hazardous Trace Elements in the Drainage from High-Sulfur Coal Preparataion Wastes," in preparation). The technique can be made quantitative for specific elements by incorporating isotope-dilution techniques at the expense of increased analysis time. Without isotope-dilution, the reliability is about a factor of 3 for most trace elements. In certain cases, the reliability is not even this good [E. D. Estis, F. Smith, and D. E. Wagoner, "Level I Environmental Assessmental Performance Evaluation," EPA-600/7-79-032 (1979)].

We initiated the use of spark source mass spectrometry in 1979. A chemical treatment has been developed to destroy organic material that otherwise interferes over the whole atomic mass region and above 200 amu. A major effort is underway to establish sensitivity factors for about 70 elements at selected operating conditions to attain improved reliability. The more quantitative measurement technique of line-density photometry coupled with emulsion calibration is being used, rather than the "disappearing line" technique. Appendix N presents early results and the technique used for an analysis of NBS SRM 1632 coal. This and other reference materials, interlaboratory exchange samples, and routine samples will be analyzed in the future, using more reliable sensitivity factors.

F. "Standard" Coal Waste Leachate

Over the years we have leached a number of high-sulfur coal waste materials. When confronted with evaluating control technologies for cleaning up these leachates, we leached large quantities of waste materials to give us samples that represented real world models. This process was slow, as large quantities had to be shaken and filtered. The filters readily clogged, which made a tedious mess. To remedy this problem, we have formulated an artificial leachate for future use where high-sulfur coal-waste leachates are needed.

The recipe representing a slightly weathered leachate in which the ferrous:ferric ratio is 2:1 is given in Table XXX. The $Fe_2(SO_4)_3$ is dissolved in 6 ℓ of Milli-Q water, the Na_2SO_4 is dissolved in 2 ℓ of water, and each is added to a 12-gal. carboy. The last 12 compounds (from $CdSO_4$ to H_2SO_4) are dissolved in 500 mℓ of water. The NaF and Na_3PO_4 are dissolved in water together and acidified with the acid solution above. The $MgSO_4$ is dissolved in several liters of water and added

TABLE XXX

RECIPE FOR SYNTHETIC, HIGH-SULFUR COAL WASTE LEACHATE

Formula	Name[a]	Weight in 40ℓ(g)	Trace Metal ppm	Trace Metal mole/ℓ[b]
$FeSO_4 \cdot 7H_2O$	Ferrous Sulfate	876	4400	7.88×10^{-2}
$Fe_2(SO_4)_3 \cdot xH_2O$ [72%]	Ferric Sulfate	438	2200	3.94×10^{-2}
$CaCO_3$	Calcium Carbonate	49.9	500	1.25×10^{-2}
$Al_2(SO_4)_3 \cdot 18H_2O$	Aluminum Sulfate	267	540	2.00×10^{-2}
$MgSO_4$	Magnesium Sulfate	15.9	80	3.30×10^{-3}
$Na_3PO_4 \cdot 12H_2O$	Sodium Phosphate Tribasic	17.2	39	1.25×10^{-3}
NaF	Sodium Fluoride	11.6	131	6.90×10^{-3}
Na_2SO_4	Sodium Sulfate	34.0	-	(5.98×10^{-3})
$Cr_2(SO_4)_3 \cdot 15H_2O$	Chromic Sulfate	0.102	0.40	7.70×10^{-6}
$CdSO_4$	Cadmium Sulfate	0.0036	0.049	4.32×10^{-7}
$CoCl_2$	Cobaltous Chloride	1.62	12	1.70×10^{-4}
$CuSO_4$	Cupric Sulfate	0.0148	0.15	2.32×10^{-6}
$MnSO_4 \cdot 4H_2O$	Manganous Sulfate	2.44	22	4.04×10^{-4}
MoO_3	Molybdenum Oxide	0.0180	0.30	3.12×10^{-6}
$NiSO_4$	Nickelous Sulfate	3.04	29	4.91×10^{-4}
H_3AsO_4	Arsenic Acid	0.182	3.0	1.98×10^{-5}
K_2SO_4	Potassium Sulfate	2.50	28	7.17×10^{-4}
$Na_2B_4O_7 \cdot 10H_2O$	Sodium Borate	0.812	2.3	2.13×10^{-4}
$ZnSO_4$	Zinc Sulfate	4.75	27	4.13×10^{-4}
$PbSO_4$	Lead Sulfate	0.0029	0.05	2.39×10^{-7}
H_2SO_4 [96%]	conc. Sulfuric Acid	68.6	-	(1.68×10^{-2})
Na^+	Sodium Ion		520	2.27×10^{-2}
$SO_4^{=}$	Sulfate Ion		18 800	1.96×10^{-1}
Cl^-	Chloride Ion		12	3.40×10^{-4}

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[a] Trace metal underlined; Milli-Q water used.

[b] Value in parentheses is molar concentration of compound used.

to this acid mixture, which is then added to the carboy. (Heating and stirring may be required before adding it to the carboy, if a precipitate forms.) The $Cr_2(SO_4)_3$ is dissolved in 1 ℓ of boiling water and added to the carboy. The $FeSO_4$ is dissolved under argon or nitrogen in 6 ℓ of water. The carboy is purged with inert gas, and the $FeSO_4$ solution is added. The $Al_2(SO_4)_3$ is dissolved in 2 ℓ of water and added to the carboy. Finally, the $CaCO_3$ is added to the carboy as a water slurry, and the remainder of the water (to make up 40 ℓ) is added. The carboy is swirled to mix, and the liquid is stored under inert gas to preserve it.

To simulate a leachate which has had little weathering, the amount of ferric ions is drastically reduced. To keep the acidity constant, the H_2SO_4 content is increased. Using the following amounts in place of those in Table XXX will produce a leachate in which the ferrous ions account for 95 percent of the iron ions. More water is used to dissolve the ferrous sulfate. Again the solution must be protected from air.

Formula	Compound	g/40ℓ	Metal Level (ppm)
$FeSO_4$	Ferrous sulfate	1248	6270
$Fe_2(SO_4)_3 \cdot xH_2O$ [72%]	Ferric sulfate	65.7	330
H_2SO_4 [96%]	conc. Sulfuric acid	137.3	
$SO_4^{=}$	Sulfate ions		18500

PERSONNEL

A large number of LASL personnel besides the authors participated in the programmatic effort during the year. Their work and contributions are gratefully acknowledged.

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APPENDIX A

EFFECTS OF TEMPERATURE AND ADDITIVES ON SULFUR RETENTION AND AQUEOUS TRACE ELEMENT RELEASES FROM CALCINED COAL WASTE

I. CALCINING PROCEDURE*

Prepared mixtures were placed in a porcelain dish and heated (normally for 2 h) in a muffle furnace preheated to the desired temperature. The calcined products usually sintered above 800°C, but were friable. Samples were ground for leaching and analyses. Mixtures calcined and their sulfur-retention values are given in Table A-I.

II. CARBONATE TREATMENT

A. Dry Mixing

Ground (-20 mesh or -10+32 mesh), Plant C, average coal waste was tumbled together for 1 hour with powdered (-115 mesh) AR grade calcium carbonate or pulverized (-10+32 mesh) Jemez limestone. If additives, such as powdered (-115 mesh) ferric oxide and granular (-35 mesh) sodium chloride, were used, they were blended at the same time.

B. Slurry Mixing

Similar to above except that a creamy paste of calcium carbonate was slurried with the waste in a porcelain dish. The paste was dried overnight on a steam bath. Without being disturbed, the mass was calcined.

III. AQUEOUS LEACHING

Calcined waste (20 - 25 g and free flowing) was leached for 48 h with distilled water (1 waste:4 water) in a beaker. In several cases, dilute sulfuric acid solutions were used as leaching agents. Agitation was provided by a magnetic stirring bar and motor. The leachates were separated by vacuum filtration through Whatman #2 paper. Filtration through #42 paper produced the leachate that was analyzed for trace elements. Trace element levels in the leachates are reported in Table A-II.

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*Another procedure in which 3/8 in or 3/8 x 0 waste was burned in flowing air for 6 h in a quartz tube heated to 800-850°C is reported on p. 8 of our third annual report (LA-7831-PR). Levels of elements retained and trace elements leached from columns of burned waste are reported there also.

TABLE A-I

SULFUR RETENTION UPON CALCINING TREATED AND UNTREATED COAL WASTE

CAL No.	Temp (°C)	Time (h)	Size (mesh)	Wt (g)	$CaCO_3$ Source[a]	Additive[b]	Ca/S (mole/mole)	Sulfur Retained in Waste (%)
29	1100	2	-20	25	AR	-	0.5	<0.1
13,14	1000	2	-20	50	-	-	0	2.2
19,20	"	"	"	25	AR	-	0.5	22
30	"	"	"	30	"	-	1.0	32
31	"	"	"	30	"	-	1.5	33
24	900	2	-20	25	AR	-	0.5	32
59	"	"	"	30	"	8% NaCl	"	19
25	"	4	"	25	"	-	"	44
36	"	"	"	30	"	-	"	29
26	"	6	"	25	"	-	"	44
27	"	12	"	25	"	-	"	38
46	"	2	"	30	"	-	1.0	50
58	"	2	"	30	"	-	1.5	64
32	800	2	-20	30	AR	-	0.25	32
33	"	"	"	30	"	-	0.5	53
51	"	"	"	30	"	4% Fe_2O_3	"	49
60	"	"	"	30	"	4% NaCl	"	32
55	"	"	-10+32	30	"	-	"	42
56	"	"	"	30	"	(Slurry)	"	57
34	"	"	-20	30	"	-	0.75	71
35	"	"	"	30	"	-	1.0	79
45	"	"	"	30	"	-	"	64
47	"	"	"	30	"	-	"	67
52	"	"	"	30	"	4% Fe_2O_3	"	68
61	"	"	"	30	"	4% NaCl	"	50
53	"	"	-10+32	30	Jemez	-	"	43
38	"	"	-20	30	AR	-	1.5	74
54	"	"	-10+32	30	Jemez	-	"	48
66	"	"	"	30	"	-	2.0	52
67	"	"	"	30	"	-	"	54
68	"	"	"	30	"	-	2.5	53
69	"	"	"	30	"	-	"	60
37	600	2	-20	30	AR	-	0.5	44
48	"	"	"	30	"	4% Fe_2O_3	"	37
62	"	"	"	30	"	4% NaCl	"	45
39	"	"	"	30	"	-	1.0	55
49	"	"	"	30	"	4% Fe_2O_3	"	52
63	"	"	"	30	"	4% NaCl	"	58
40	"	"	"	30	"	-	1.25	53
41	"	"	"	30	"	-	1.5	68
50	"	"	"	30	"	-	"	69

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[a] AR = AR grade $CaCO_3$ powder;
Jemez = -10+32 mesh Jemez, NM limestone.

[b] Percentage based on $CaCO_3$ level.

TABLE A-II

TRACE ELEMENT CONCENTRATIONS IN LEACHATES FROM CALCINED COAL WASTES[a]

Temp(°C)	Time(h)	Particle Size[b]	Ca/S[c]	Leachate[d]	pH	TDS(%)	Al	Ca	Cd	Co	Cr	Cu	F	Fe	K	Mn	Na	Ni	Zn
Control	0	-20	0	Water	2.9	0.63	100	550	0.06	2.8	0.068	0.10	14	600	14	5.8	76	4.8	2.8
Control	0	-10+32	0	Water	3.2	0.51	48	360	<0.0003	1.3	0.060	0.20		520		5.0		4.2	1.8
600	2	-20	0	Water	6.6	0.38	<0.8	610	0.005	0.1	<0.0003	0.18	0.5	<0.05	7	4.2	73	0.08	0.35
800	2	-20	0	Water	6.9	0.33	0.38	560	0.0008	0.25	0.025	0.14		0.5		3.2		0.3	0.43
"	"	"	0	"	7.0	0.36	0.45	580	0.0008	0.23	0.025	0.16		0.13		2.9		0.25	0.48
"	"	"	0	"	7.0	0.35	0.4	570	0.0008	0.24	0.019	0.15		0.32		3.0		0.28	0.46
"	"	"	1.0	"	12.4	0.34	0.6	900	<0.0002	0.03	0.016	0.21		0.05		0.03		0.13	0.11
900	4	-20	0.5	Water	10.5	1.6	0.3	820	0.0006	0.06	<0.013	0.30		0.09		0.06		0.13	0.17
1000	2	-20	0	Water	8.0	0.17	0.4	400	0.0002	<0.01	0.001	0.01	1	<0.03	9.3	0.03	12	0.01	0.05
"	"	"	0	"	7.9	0.17	<0.4	400	0.0003	<0.01	0.003	0.01	1	<0.03	9.5	0.03	12	0.01	0.08
"	"	-10+32	0	"	8.3	0.11	<0.3	240	0.023	<0.03	<0.03	0.14		0.05		<0.03		<0.03	0.15
"	"	-20	0	0.02M H_2SO_4	4.0	0.4	5	620	<0.008	0.04	<0.03	0.13	5.5	13	15	0.90	15	0.15	4.0
"	"	"	0	0.04M H_2SO_4	2.9	0.5	88	580	<0.006	0.05	<0.04	0.20	40	25	25	1.2	30	0.15	3.8

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[a] Element values in ppm.

[b] Values are meshes.

[c] Calcium-to-sulfur molar ratio.

[d] 48h leach, 4 mℓ leachate per gram of waste.

APPENDIX B

MORTARS FROM FINE COAL PREPARATION WASTE

I. CEMENT CYLINDER PRODUCTION.

Formulas were dry mixed, treated with water until workable, and poured into 3.2-cm Silastic molds. Setup occurred overnight to give a damp, scratchable cylinder. Curing in Los Alamos air (normally 10% humidity) continued after the cylinders were removed from the mold until they were leached. Controls used: -10 mesh river sand. Test samples used: -20 mesh, Plant C, high-sulfur, coal waste. Cylinders were normally 1 in high.

II. CYLINDRICAL SPECIMENS

Sample No.	Portland Cement	Hydrated Lime	Type	Portion	Weight (g)	Cylinder Size (cc)*	Leaching Comments
CM-4	1	1/2	Sand	3	30	18	Control
CM-5	1	1/2	Waste	3	30	18	
CM-6	1	1/2	Waste	6	30	18	Very slight spalling on 19th day
CM-7	1	1/2	Waste	6	60	60	Hardened plug broke into pieces <3/8 in.
CM-9	1	1/2	Waste	12	60	18	Disintegrated in less than 1 hour
CM-10	1	0	Waste	6	30	18	Disintegrated in less than 1 min +20 mesh leached
CM-13	1	1/2	Waste	6	30	18	Same as CM-6

*18cc size is 2.5 cm high by 3 cm diam.

III. LEACHING

Cylinders were placed on a platform in tap water, which was slowly stirred to minimize erosion. Leachates were periodically changed. The leachate was analyzed without filtering. The pH values of leachates for cylinders labeled CM-4, CM-5 and CM-6 are plotted versus time in Fig. B-1. Trace element releases are described in Table B-1.

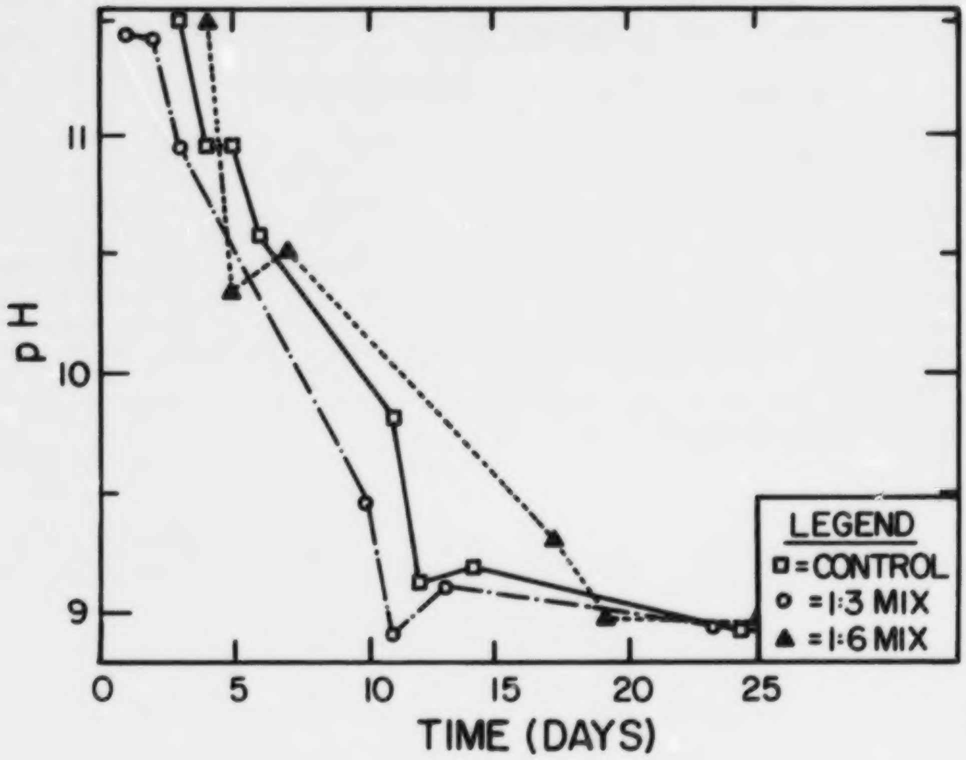

Fig. B-1.
The pH of leachates in contact with mortar cylinders from fine aggregate coal waste. (leachate changed before each pH drop.)

TABLE B-I

TRACE ELEMENT RELEASES FROM CEMENT/COAL WASTE CYLINDERS[a]

Parameter	CM-7	CM-13
Waste Mass (cc)	60	18
Leachate Vol (ml)	250	250
Length of Leach (days)	128.[b]	120.[c]
pH (initial)	12.2	11.3
pH (final)	11.2	9.0
Al	0.10	0.13
As	5	3
Ca	250	1
Cd	<0.05	<0.05
Co	0.02	0.01
Cr	0.008	<0.004
Cu	0.10	0.08
Fe	0.05	0.03
Mn	0.05	<0.008
Ni	0.04	0.01
Zn	0.05	0.04

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[a] Elemental concentrations in ppm, except Cd, which is in ppb.

[b] Four 250-mℓ leaches in the first 55 days. Trace element results are for the fifth leachate, which was in contact with cylinder for 73 days.

[c] Four 250-mℓ leaches in the first 44 days. Trace element results are for the fifth leachate.

APPENDIX C

LIME/LIMESTONE TREATMENT OF COAL WASTE

The first experiments in this series were reported in the third annual report. They included the dry-mixing series designated GL-12 to GL-17 (Appendix C, LA-7831-PR) and the slurry-mixing series marked CTWT-11-1 to CTWT-11-5 (Appendix D, LA-7831-PR). The experiments here, CTWT-11-6 to CTWT-11-9, are extensions of the CTWT, slurry-mixing series. Salient items are presented in Table C-I for the entire series.

I. MIXING PROCEDURE

Average coal preparation waste (-3/8 in) from Plant B was added to a 2-ℓ beaker containing a slurry of neutralizing agent (see CTWT-11-6 to CTWT-11-9 in Table C-I) with hand stirring for 1/2 h. In several cases the slurry was allowed to soak. In one, carbon dioxide was bubbled in until the mixture was neutral. Drying was accomplished with Los Alamos' 10% humidity with a forced air oven at 60°C. The friable mass was passed through a -3/8-in jaw crusher to return it to the original waste size.

II. LEACHING

The treated waste was packed in a 4.6-cm I.D. by 40-cm-long glass column containing a glass wool plug at the bottom. Distilled water was passed upward through the column at 0.5mℓ/min. Leaching was halted after approximately 8 ℓ. The columns were drained and aired for 20 days. Leaching was then resumed. Trace element data are reported in Tables C-II to C-V.

TABLE C-I

SUMMARY OF COAL WASTE-ALKALINE AGENT SLURRY EXPERIMENTS[a]

NEUTRALIZING AGENT ADDITIVE	NEUTRALIZING AGENT SIZE	NEUTRALIZING AGENT (%)[b]	TYPE OF MIXING	COMMENTS	EFFLUENT pH INITIAL	EFFLUENT pH AFTER AIRING	DAYS AIRING[c]	EFFLUENT Fe (ppm) INITIAL	EFFLUENT Fe (ppm) AFTER AIRING	SAMPLE NO.
None	–	0.0	–	Control	1.3	1.7	28[d]	15000	7600	GL–12
Limestone	–3/8 in.	16.9	Dry	Evenly mixed	2.5	3.2	28[d]	8100	940	GL–14
Limestone	–3/8 in.	17.0	Dry	Placed at water inlet	1.5	3.6	28[d]	10400	1400	GL–15
Limestone	–3/8 in.	17.6	Dry	Placed at water outlet	2.4	–	–	10700	–	GL–16
Limestone	–20 mesh	16.9	Dry	Placed at water outlet	3.5	–	–	7800	–	GL–17
None	–	0.0	–	Control; wetted; 24h @ 60°C	1.8	2.2	14[d]	13200	700	CTWT–11–1
$Ca(OH)_2$	–100 mesh	0.5	Slurry	1/2h mix; 24h @ 60°C	2.1	2.2	14[d]	10750	1020	CTWT–11–2
$Ca(OH)_2$	–100 mesh	1.5	Slurry	1/2h mix; 24h @ 60°C	2.6	2.3	14[d]	2820	1980	CTWT–11–3
$Ca(OH)_2$	–100 mesh	3.0	Slurry	1/2h mix; 24h @ 60°C	6.6	2.8	14[d]	120	700	CTWT–11–4
$Ca(OH)_2$	–100 mesh	10.0	Slurry	1/2h mix; 24h @ 60°C	13.0	10.7	14[d]	<0.1	<0.1	CTWT–11–5
$Ca(OH)_2$	–100 mesh	5.0	Slurry	1/2h mix + CO_2 for 3 days; 24h @ 60°C	7.4	5.8	20[e]	5	23	CTWT–11–6
$CaCO_3$	–100 mesh	6.7	Slurry	1/2h mix; soak for 3 days; 24h @ 60°C	6.9	7.3	20[e]	15	0.7	CTWT–11–7
$Ca(OH)_2$ + $CaCO_3$	–100 mesh –100 mesh	1.5 4.0	Slurry	1/2h mix of lime; then 1/2h mix $CaCO_3$; 24h @ 60°C	6.2	3.8	20[e]	130	210	CTWT–11–8
Limestone	–20 mesh	6.0	Slurry	24h soak; 24h @ 60°C	6.4	4.6	20[e]	60	100	CTWT–11–9

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[a] 1500 grams of combined material leached in GL series and CTWT–11–1 to 11–5; 500 grams of material used in CTWT–11–6 to 11–9; –3/8" waste used in all cases.

[b] Based on waste.

[c] Leaching stopped after x liters of leachate; column drained and air circulated through column.

[d] Air started after ~4 liters; first 3 days with dry air, then remainder with H_2O saturated air.

[e] Air started after ~8 liters; first week with dry air, then remainder with H_2O saturated air.

TABLE C-II

TRACE ELEMENT LEVELS IN LEACHATES FROM COAL WASTE SLURRIED WITH LIME WHICH WAS THEN NEUTRALIZED WITH CARBON DIOXIDE[a]

Sample No.	1	2	4	11	17	31[b]	33	34
Vol (ℓ)	0.100	0.201	0.697	2.309	3.326	8.826	9.002	9.107
pH	7.4	7.2	7.9	7.7	7.7	5.8	6.4	6.9
TDS (%)	0.84	0.63	0.34	0.27	0.22	0.29	0.27	0.21
F	0.3	0.4	0.3	0.3	0.4	0.3	0.4	0.2
Na	7	6	2.5	1	1	5	2	2
Al	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
K	7	8	4	2	1	6	4	4
Ca	900	870	630	540	480	560	470	400
Cr (μg/ℓ)	<0.5	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Mn	0.7	0.5	0.2	0.1	0.07	1.5	1.4	0.8
Fe	5	2	0.4	<0.3	<0.3	23	17	5
Co	0.13	0.12	0.06	0.05	<0.05	0.4	0.3	0.25
Ni	0.3	0.2	0.2	0.1	<0.07	0.7	0.5	0.4
Cu	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	0.07	0.07	0.03	0.01	<0.01	0.3	0.2	0.1
Cd (μg/ℓ)	2	1	0.4	0.2	0.3	2	1	0.6

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[a] Values in μg/mℓ unless otherwise noted.

[b] After column "air-regenerated".

TABLE C-III

TRACE ELEMENT LEVELS IN LEACHATES FROM A COAL WASTE SLURRIED WITH FINE-PARTICULATE CALCIUM CARBONATE[a]

Sample No.	1	2	4	12	18	31[b]	34
Vol (ℓ)	0.101	0.155	0.641	2.298	4.622	8.813	9.098
pH	6.9	7.5	7.1	7.5	7.7	7.3	7.2
TDS (%)	0.38	0.39	0.37	0.23	0.18	0.19	0.18
F	0.2	0.2	0.05	0.15	0.19	0.14	0.14
Na	14	12	5	1.5	1	4	2
Al	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
K	10	8	5	2	1	3	2
Ca	650	620	610	540	370	320	330
Cr (μg/ℓ)	<0.5	<0.5	<0.5	<0.5	<0.5	1	<0.5
Mn	2	2	0.4	0.09	<0.05	0.09	0.08
Fe	15	12	<0.3	<0.3	<0.3	0.7	0.5
Co	0.3	0.3	0.1	0.05	<0.05	0.05	0.05
Ni	0.8	0.8	0.3	0.07	<0.07	0.1	0.1
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	0.06	0.06	<0.01	0.03	0.03	0.04	0.01
Cd (μg/ℓ)	3	2	<0.05	0.1	<0.05	0.4	0.4

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[a] Element concentrations in μg/mℓ, unless noted.

[b] Column drained and aired for 20 days; then leaching resumed.

TABLE C-IV

TRACE ELEMENT LEVELS IN LEACHATES FROM A COAL WASTE SLURRIED WITH LIME FOLLOWED BY CALCIUM CARBONATE[a]

Sample No.	1	2	4	11	17	25[b]	26	27	28
Vol(ℓ)	0.088	0.174	0.689	2.327	3.953	8.237	8.325	8.413	8.508
pH	6.2	6.3	6.4	7.1	7.3	3.8	4.2	4.4	4.9
TDS (%)	0.45	0.23	0.37	0.32	0.24	0.41	0.40	0.33	0.29
F	0.14	0.14	0.16	0.18	0.29	0.30	0.26	0.21	0.17
Na	11	10	4	1.5	1	6	5	4	4
Al	<0.5	<0.5	<0.5	<0.5	<0.5	5	4	2	0.9
K	7	6	5	2	2	7	6	6	5
Ca	600	590	650	610	570	570	550	510	480
Cr (μg/ℓ)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Mn	6	5	2	0.2	0.2	1	0.8	0.7	0.5
Fe	130	155	64	1	<0.3	210	190	170	120
Co	1.4	1.2	0.2	0.05	<0.05	1	0.8	0.6	0.5
Ni	2.4	2.0	0.6	0.1	0.08	1.5	1.3	1	0.8
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1	<0.1
Zn	0.4	0.4	0.1	0.02	0.02	0.6	0.3	0.2	0.2
Cd (μg/ℓ)	6	5	0.7	0.2	0.2	13	11	7	15

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[a] Elemental concentrations in μg/mℓ, unless noted.

[b] Column drained and aired for 20 days; then leaching resumed.

TABLE C-V

TRACE ELEMENT LEVELS IN LEACHATES FROM A COAL WASTE SLURRIED WITH A GROUND LIMESTONE [a]

Sample No.	1	5	14	15	31[b]	33	34
Vol (ℓ)	0.208	0.538	2.218	5.308	8.422	8.598	8.675
pH	6.4	6.4	7.2	7.8	4.6	5.4	6.2
TDS (%)	0.14	0.30	0.20	0.35	0.28	0.25	0.24
F	0.15	0.16	0.18	0.20	0.18	0.14	0.15
Na	6	4	2	1	22	4	3
Al	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
K	4	3	2	1	6	5	4
Ca	610	590	420	290	620	580	470
Cr (μg/ℓ)	1	<0.5	6	<0.5	<0.5	0.5	1
Mn	2	1	0.2	0.1	1	0.7	0.6
Fe	60	27	1.	0.6	100	50	19
Co	0.4	0.2	<0.05	<0.05	0.6	0.3	0.2
Ni	0.9	0.4	0.08	<0.07	1	0.8	0.6
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	0.1	0.06	0.04	0.01	0.07	0.19	0.04
Cd (μg/ℓ)	2	0.8	2	0.05	6	7	2

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[a] Elemental concentrations in μg/mℓ, unless noted.

[b] Column drained and aired for 20 days; then leaching resumed.

APPENDIX D

ATTENUATION OF SEVERAL TRACE ELEMENTS IN A COAL WASTE LEACHATE BY SOLID MATERIALS - SUCCESSIVE INCREMENT METHOD

A 2:1 weight ratio of leachate (CTWT-1012; see the section on "Freshwater Algae" in Appendix K for trace element data) solids was shaken overnight at ninety 3-1/2-in. strokes per minute. (A list of the solids, along with several of their properties, is given in Table D-I). This slurry was vacuum-filtered through Whatman 42 paper and then gravity-filtered through Whatman 42 paper. Where initial filtration was not possible because of clogging, high speed (15000 rpm) centrifugation was substituted for the vacuum filtration. Part of the resultant filtrate was taken for analyses, and the remainder was diluted to a volume sufficient to continue and equilibrated with fresh solid material in a 2:1 ratio. Up to six successive equilibration cycles were performed in this manner for each solid material. Control equilibrations were performed with distilled water and 0.136M H_2SO_4 (equivalent in total acidity of the initial coal refuse leachate).

The analytical results for pH and trace element contents of the filtrates are given in Table D-II.

TABLE D-I

SOLID SORBENTS USED IN SUCCESSIVE INCREMENT, BATCH EXPERIMENTS

Material	Comment	Carbonate[a] (%)	Cation Exchange Capacity[b] (meq/100g)	Clay[c] (%)	Organic Matter[d] (%)	pH[e]	Number of Equilibrations
Alluvial Soil	Weathered Partly Calcareous	1.65	26.1	48	0.7	7.8	3
Glacial Till Soil	Unweathered Calcareous	15.1	9.1	13.5	0.4	7.6	6
Glacial Till Soil	Weathered Leached	0.3	28.0	17.0	0.3	7.3	4
Loess Soil	Weakly Weathered Leached	0.45	9.8	10.8	0.2	7.3	3
Loess Soil	Unweathered Calcareous	8.3	8.8	9.5	0.3	7.6	5
Organic Soil	Weakly Weathered Calcareous	6.8	30.3	38.6	7.3	7.6	3
Kaolinite Clay		0.48	21.4	-	0.3	8.2	6
Montmorillonite Clay		0.54	115	-	0	7.7	6
Precipitator Ash	Highly Alkaline	1.2	3.0	1.5	0.3	11.2	6
Scrubber Sludge	Limestone Scrubber	30.0	2.7	6.3	3.7	8.1	4
Calcium Carbonate	Reagent Grade	60.0	—	—	-	7.4	6

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[a] Carbonate by rapid titration method.
[b] Cation exchange capacity by ammonium acetate extraction following sodium acetate saturation.
[c] Clay by pipet sedimentation.
[d] Organic matter by Walkley-Black procedure.
[e] pH of water-soil filtrate after equilibration for 16 h.

TABLE D-II

TRACE ELEMENT ATTENUATIONS BY SUCCESSIVE TREATMENTS WITH SOILS AND ALKALINE SOLIDS[a]

Attenuating Material	Comment	Liquid	Attenuation Step	pH	F	Al	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd
None	Ferrous Leachate	Initial Leachate	NA	2.0	128	350	530	0.57	16	1100	8	12	0.2	23	0.81	0.3
Alluvial Soil	Weathered Partly Calcareous	H_2O	NA	7.8	0.8	<0.1	28	<0.01	<0.02	0.1	<0.02	<0.02	<0.02	0.01	<0.002	<0.01
		Leachate	1	4.8	21	16	470	<0.01	150	200	5	9	<0.03	13	<0.003	0.19
			2	7.2	1.8	<0.1	750	<0.02	80	0.1	0.2	0.5	<0.04	0.07		<0.02
			3	8.1	0.8	<0.1	560	<0.01	5	0.1	<0.02	<0.02	<0.02	<0.01	0.006	<0.01
		0.14M H_2SO_4	NA	6.0	0.8	[illegible]	560	<0.01	5	0.1	<0.02	<0.02	<0.02	<0.01	0.006	<0.01
Glacial Till Soil	Unweathered Calcareous	H_2O	NA	7.8	1	<0.1	23	<0.01	0.02	[illegible]	<0.02	<0.02	<0.02	0.01	<0.002	<0.01
		Leachate	1	6.3	130	[illegible]	540	<0.01	40	1120	5	8	<0.02	7	<0.002	0.06
			2	7.8	3.3	<0.1	780	<0.02	31	0.1	0.2	0.5	<0.05	0.01		<0.02
			3	8.0	12	<0.2	780	<0.02	0.8	[illegible]	<0.03	<0.03	<0.03	<0.02	0.012	<0.02
			4	8.0	1.8	<0.1	670	<0.03	0.3	0.1	<0.07	<0.07	<0.07	0.01	<0.007	<0.03
			5	8.3	13	<0.004	840	<0.04	0.35	0.1	<0.2	<0.08	<0.08	0.04	<0.009	<0.04
			6	7.8	9	<0.004	840	<0.04	80	0.1	<0.08	<0.08	<0.08	<0.04	<0.008	<0.04
		0.14M H_2SO_4	NA	6.4	0.8	<0.1	720	0.01	5	[illegible]	<0.02	<0.02	<0.02	[illegible]	<0.001	<0.01
Glacial Till Soil	Weathered Leached	H_2O	NA	7.3	0.9	<0.1	18	0.01	<0.02	[illegible]	<0.02	<0.02	<0.02	0.01	<0.002	0.01
		Leachate	1	3.8	48	420	690	0.1	290	3200	7	11	0.4	24	0.31	0.3
			2	4.0	17	60	730	0.02	420	1230	6.6	6.6	0.07	11	0.024	0.2
			3	6.7	1.4	[illegible]	1020	<0.02	340	1.1	2.3	2.3	<0.05	1.1	0.007	0.05
			4	7.2	1.2	[illegible]	1040	<0.006	37	[illegible]	<0.12	<0.12	<0.12	0.2	0.05	<0.06
		0.14M H_2SO_4	NA	2.0	8	[illegible]	540	0.75	80	[illegible]	0.7	1	0.2	3	0.030	<0.01
Loess Soil	Weakly Weathered Leached	H_2O	NA	7.0	0.5	[illegible]	4	<0.01	<0.02	0.2	<0.02	<0.02	0.02	0.01	<0.002	0.05
		Leachate	1	2.7	4.4	350	510	0.6	140	4000	7	13	1	22	0.297	0.3
			2	3.4	78	200	520	0.2	200	1250	8	11	1.3	18	0.105	0.3
			3	4.0	52	360	410	0.02	260	2100	8	8	0.8	16	<0.004	0.40
		0.14M H_2SO_4	NA	7.8	24	4800	500	1.1	47	4.5	0.7	2	0.8	1	0.045	0.05
Loess Soil	Unweathered Calcareous	H_2O	NA	7.6	0.8	<0.1	20	<0.01	<0.02	[illegible]	<0.02	<0.02	<0.02	0.01	<0.002	0.01
		Leachate	1	4.8	69	9	510	<0.01	110	900	6	12	0.3	25	<0.002	0.2
			2	5.9	12	6	880	<0.02	170	640	5	8	0.03	8	<0.003	0.2
			3	7.4	3.1	<0.1	1120	<0.02	150	0.48	0.9	1.5	<0.03	0.2	<0.006	0.02
			4	7.8	1.5	<0.4	1180	<0.04	45	[illegible]	<0.08	0.11	<0.08	<0.04	<0.008	<0.04
			5	8.0	1.9	<0.4	1170	<0.04	1.8	[illegible]	<0.08	<0.08	<0.08	0.08	0.008	<0.04
		0.14M H_2SO_4	NA	6.2	1	[illegible]	560	<0.01	5	0.08	<0.02	0.04	<0.02	0.01	0.021	<0.01
Organic Soil	Weakly Weathered Calcareous	H_2O	NA	7.8	0.4	[illegible]	330	<0.01	1	0.08	<0.02	<0.02	<0.02	0.02	0.017	<0.01
		Leachate	1	6.6	4.1	[illegible]	560	<0.01	48	780	1.3	1.1	<0.01	2.3	<0.003	<0.01
			2	7.7	1.4	[illegible]	1080	<0.02	15	[illegible]	0.06	<0.01	<0.01	0.14	<0.003	<0.02
			3	8.0	1.2	[illegible]	1180	<0.03	6	1.8	<0.08	<0.08	0.08	0.01	<0.008	<0.03
		0.14M H_2SO_4	NA	6.4	[illegible]	[illegible]	650	<0.01	6	0.2	<0.02	<0.02	<0.02	0.01	<0.002	<0.01
Kaolinite Clay		H_2O	NA	8.2	1.3	1	24	<0.01	<0.02	0.08	<0.02	<0.02	0.02	<0.01	0.009	<0.01
		Leachate	1	4.2	41	170	510	<0.02	27	800	3.9	12	2	20	<0.004	0.4
			2	7.4	1.8	0.8	1310	<0.04	12	0.8	0.3	0.8	<0.08	0.08	<0.004	0.04
			3	8.0	2	[illegible]	1180	<0.05	0.2	4.7	<0.10	<0.01	0.21	[illegible]	<0.004	<0.05
			4	8.0	1	[illegible]	880	<0.07	<0.15	[illegible]	<0.15	<0.15	<0.25	<0.07	<0.014	<0.07
			5	8.7	9	[illegible]	950	<0.13	<0.25	[illegible]	<0.25	<0.25	0.4	[illegible]	<0.025	<0.13
			6	7.8	100	[illegible]	1080	<0.13	<0.25	[illegible]	<0.25	<0.25	0.5	[illegible]	<0.025	<0.13
		0.14M H_2SO_4	NA	3.8	11	240	810	0.58	17	81	1.3	[illegible]	[illegible]	0.8	<0.003	0.10
Montmorillonite Clay		H_2O	NA	7.7	0.8	1.8	12	<0.02	<0.01	[illegible]	<0.03	<0.03	<0.03	<0.02	<0.003	<0.02
		Leachate	1	3.7	19	[illegible]	530	0.08	51	540	0.82	1.6	<0.04	[illegible]	<0.004	0.06
			2	6.8	0.15	[illegible]	1100	<0.04	1.3	[illegible]	<0.07	<0.07	<0.07	[illegible]	<0.007	<0.04
			3	7.8	0.08	[illegible]	1050	<0.05	<0.10	[illegible]	<0.1	<0.1	<0.1	[illegible]	<0.008	<0.05
			4	7.8	1.0	[illegible]	1180	<0.11	<0.21	[illegible]	<0.21	<0.21	<0.21	<0.11	<0.022	<0.11
			5	8.1	4.1	[illegible]	1070	<0.21	<0.41	<0.41	<0.41	<0.41	<0.41	<0.21	<0.042	<0.21
			6	7.5	23.4	[illegible]	1250	<0.21	<0.41	[illegible]	<0.41	<0.41	<0.41	[illegible]	<0.042	<0.21
		0.14M H_2SO_4	NA	3.8	9.4	30	530	0.05	2	1	<0.02	<0.02	<0.02	0.2	0.08	<0.01
Precipitator Ash	Highly Alkaline	H_2O	NA	10.2	3.3	[illegible]	70	0.13	<0.02	[illegible]	<0.02	<0.02	<0.02	0.1	0.050	0.06
		Leachate	1	4.4	100	140	500	0.01	14	1120	8	13	0.2	24	<0.002	0.3
			2	7.0	8	[illegible]	370	<0.01	90	[illegible]	3	5	<0.03	0.8	<0.005	0.03
			3	9.8	[illegible]	[illegible]	700	0.3	[illegible]	[illegible]	<0.03	0.03	<0.03	[illegible]	0.158	<0.01
			4	10.2	2.1	[illegible]	670	0.5	<0.05	[illegible]	<0.05	<0.05	<0.05	[illegible]	0.072	<0.02
			5	11.0	2.9	[illegible]	920	0.9	<0.08	[illegible]	<0.08	<0.08	<0.08	[illegible]	0.072	<0.03
			6	11.0	29	8	1070	1.2	<0.08	[illegible]	<0.08	<0.08	<0.08	[illegible]	0.110	<0.03
		0.14M H_2SO_4	NA	3.7	41	[illegible]	520	0.06	24	8	0.1	0.2	0.8	2	0.580	0.05
Scrubber Sludge	Limestone Scrubber	H_2O	NA	8.1	7	[illegible]	600	<0.01	<0.02	[illegible]	<0.02	<0.02	0.01	[illegible]	0.006	<0.01
		Leachate	1	7.8	16	30	400	<0.02	11	2000	5	11	0.03	20	<0.003	0.5
			2	7.4	17	[illegible]	1110	<0.03	23	[illegible]	2.3	3.8	0.2	5	<0.013	0.25
			3	7.8	0.6	[illegible]	1200	<0.03	11	[illegible]	<0.05	<0.05	<0.05	[illegible]	<0.005	<0.03
			4	8.1	12	[illegible]	1500	<0.06	[illegible]	<0.1	<0.1	0.1	0.1	[illegible]	0.254	0.1
		0.14M H_2SO_4	NA	6.3	9.6	[illegible]	650	<0.02	4.6	[illegible]	0.14	0.5	<0.03	1	0.05	[illegible]
Calcium Carbonate	reagent Grade	H_2O	NA	7.4	0.2	[illegible]	2	<0.01	<0.02	[illegible]	<0.02	<0.02	<0.02	[illegible]	<0.002	<0.01
		Leachate	1	6.7	1.2	[illegible]	560	<0.01	8	1100	2.6	5	<0.01	[illegible]	<0.003	<0.01
			2	7.5	1.4	[illegible]	1170	<0.02	3	1	0.8	1.5	<0.01	[illegible]	<0.001	<0.02
			3	7.8	1.0	[illegible]	970	<0.02	0.2	[illegible]	0.4	1.5	<0.04	[illegible]	0.004	<0.02
			4	8.0	1.1	[illegible]	780	<0.03	<0.07	[illegible]	0.2	1.0	<0.07	[illegible]	<0.006	<0.03
			5	7.7	0.8	[illegible]	780	<0.05	<0.1	[illegible]	0.11	[illegible]	<0.1	[illegible]	<0.010	<0.05
			6	7.8	[illegible]	[illegible]	740	<0.05	<0.1	[illegible]	<0.1	<0.1	<0.1	[illegible]	<0.010	<0.05
		0.14M H_2SO_4	NA	6.4	[illegible]	[illegible]	760	<0.01	<0.04	[illegible]	<0.02	<0.02	<0.02	[illegible]	<0.002	<0.01

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[a] Values in μg/mℓ unless otherwise noted.

[b] After column "air-regenerated".

APPENDIX E

ATTENUATION OF SEVERAL TRACE ELEMENTS IN A COAL WASTE LEACHATE BY SOLID MATERIALS - BATCH METHOD USING DILUTED LEACHATE

Coal refuse leachate (CTWT-1012, iron concentration around 5000 ppm) was equilibrated with subsurface solids and quarry limestone which were collected from the Illinois Basin in November 1978. In addition, four Widow's Creek Power Plant solid effluents, Gallup coal, and a commercial peat were tested. A list of the materials and some of their properties is given in Table E-I.

Different dilutions of the original leachate rather than the filtrate from a previous equilibration were equilibrated overnight with fresh solid. (This gives better control of oxidation and allows some assessment of Fe++ attenuation, but does not account for previous differential attenuation.) All leachate/solid mixtures were purged about 5 minutes with argon, sealed and shaken overnight. Filtering was performed in a polyethylene chamber containing nitrogen. Filtrates were purged with nitrogen or argon gas, sealed, and stored after filtration in preparation for determining Fe++. Oxidation of Fe++ to Fe+++ was greatly retarded by these precautions. Filtrate pH, Fe++, and total Fe measurements were taken as soon as practical after filtration.

Analytical data for pH and trace elements are given in Table E-II. Plots of eluent concentration and effluent-to-influent ratios (C/C_0) for solids-to-original leachate used are given in Fig. E-1.

TABLE E-I

SOLID SORBENTS USED IN DILUTED LEACHATE, BATCH EXPERIMENTS

Material	Titratable Carbonate (%)[a]	Cation Exchange Capacity[b]	Clay[c]	Organic Matter[d]	pH[e]
Limestone Illinois Quarry	-	-	-	-	7.5
Overburden, Kentucky Seam 11	3.8	9.8	-	3.2	7.6
Overburden, Kentucky Seam 12	1.4	7.5	9.5	3.2	7.8
Loess Subsoil	0.48	24.1	22.0	1.5	4.8
Glacial Till	7.1	14.5	28.6	0.1	7.9
Western Coal	1.6	5.3	8.4	17.0	7.0
Economizer Ash	1.7	3.2	0.4	0.5	12.3
Precipitator Ash	0.6	3.0	0	0.6	11.4
FGD Scrubber Sludge	25.4	5.4	5.9	2.3	8.0
Peat	2.2	48.3	21.2	46.0	5.4
Bottom Ash	0.3	4.1	0	0	8.0

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[a] Carbonate by rapid titration method.

[b] Cation exchange capacity by ammonium acetate extraction following sodium acetate saturation.

[c] Clay by pipet sedimentation.

[d] Walkley-Black method for organic matter.

[e] pH of water-soil filtrate following 16h equilibration.

TABLE E-II

TRACE ELEMENT ATTENUATIONS OF VARIABLY CONCENTRATED LEACHATES BY SOILS AND ALKALINE SOLIDS[a]

ATTENUATING MATERIAL	COMMENT	RUN NUMBER	LEACHATE/SOLID RATIO	pH	Fe(II)	C/C_0	Fe(III)	C/C_0	F	C/C_0	Al	C/C_0	Mn	C/C_0	Ni	C/C_0	As	C/C_0
Leachate	Undiluted	NA	NA	2.0	4680	NA	260	NA	127	NA	570	NA	15.3	NA	11.6	NA	0.9	NA
Limestone	From	Water	2.0	7.5	<0.02	NA	<0.02	NA	0.7	NA	<0.2	NA	<0.01	NA	<0.02	NA	<0.001	NA
	Illinois	1	2	6.3	3640	0.78	40	0.15	6.6	5.05	1.0	0.001	12.7	0.83	8.76	0.75	0.022	0.02
	Quarry	2	0.71	7.1	96	0.059	6	0.066	3.9	0.061	<0.2		0.44	0.08	0.24	0.05	<0.001	
		3	0.40	8.0	17.6	0.019	<0.02		2.2	0.09	<0.2		0.09	0.03	0.07	0.03	0.001	0.007
		4	0.20	8.0	<0.02		<0.02		1.2	0.09	<0.2		0.03	0.02	0.02	0.01	0.002	0.02
Overburden	Calcareous	Water	2.0	7.6	<0.02	NA	<0.02	NA	1.3	NA	<0.2	NA	8.4	NA	0.18	NA	<0.002	NA
Kentucky	Slightly	1	2.0	6.0	2980	0.64	80	0.31	28.8	0.22	5.4	0.07	68.4	4.47	9.91	0.85	0.015	0.01
Seam 11	Organic	2	0.71	6.7	240	0.15	11	0.12	4.9	0.11	<0.2		35.6	6.64	1.02	0.25	0.002	0.006
		3	0.40	7.2	61	0.065	0		3.4	0.41	<0.2		23.9	7.73	0.48	0.23	<0.002	
		4	0.20	8.1	<0.02		<0.02		2.8	0.21	<0.2		13.4	8.37	0.26	0.24	0.002	0.02
Overburden	Calcareous	Water	2.0	7.8	<0.02	NA	<0.02	NA	0.9	NA	<0.2	NA	0.99	NA	<0.02	NA	<0.003	NA
Kentucky	Slightly	1	2.0	4.5	1880	0.81	80	0.31	30.6	0.70	136	0.23	36.8	2.40	11.1	0.95	0.05	0.68
Seam 12	Organic	2	0.40	6.5	419	0.45	0.0		1.8	0.07	<0.2		14.0	4.53	0.92	0.44	<0.002	
		3	0.20	7.6	3.3	0.0067	0.9	0.056	1.5	0.11	<0.2		7.9	4.93	0.18	0.16	<0.003	
		4	0.08	8.0	<0.02		<0.02		0.9	0.24	<0.2		2.70	6.00	0.02	0.05	<0.003	
Loess	Weathered	Water	2.0	4.8	<0.02	NA	<0.02	NA	<0.2	NA	2.2	NA	0.21	NA	<0.02	NA	0.005	NA
Subsoil	Leached	1	2.0	2.9	2980	0.64	140	0.54	105	0.82	566	0.99	324	21.17	11.2	0.96	0.22	0.24
	Acid	2	0.71	3.4	561	0.34	4	0.044	28.1	0.63	110	0.55	184	34.32	4.06	1.06	0.018	0.05
		3	0.40	3.7	130	0.160	1	0.019	11.3	0.47	35	0.35	108	34.95	2.06	1.00	0.011	0.07
		4	0.25	4.9	6.7	0.015	0.2	0.012	3.3	0.25	7.6	0.14	51.2	32.00	0.91	0.85	0.009	0.12
Glacial	Calcareous	Water	2.0	7.9	<0.02	NA	<0.02	NA	1.6	NA	0.7	NA	0.03	NA	<0.02	NA	<0.001	NA
Till	Unweathered	1	2.0	6.3	970	0.21	60	0.12	5.3	0.04	1.6	0.002	227	14.83	3.22	0.27	0.005	0.005
		2	1.0	7.0	72	0.011	7	0.054	2.2	0.03	<0.2		146	19.08	0.52	0.08	<0.008	
		3	0.40	7.8	<0.02		0.4	0.008	1.5	0.06	<0.2		65.6	21.22	0.16	0.07	0.004	0.02
		4	0.20	8.2	<0.02		<0.02		1.6	0.12	<0.2		17.8	11.12	0.03	0.02	0.006	0.08

[a] Element concentrations in µg/mℓ

TABLE E-II

TRACE ELEMENT ATTENUATIONS OF VARIABLY CONCENTRATED LEACHATES BY SOILS AND ALKALINE SOLIDS[a] (CONCLUDED)

ATTENUATING MATERIAL	COMMENT	RUN NUMBER	LEACHATE/SOLID RATIO	pH	Fe(II)	C/C_0	Fe(III)	C/C_0	F	C/C_0	Al	C/C_0	Mn	C/C_0	Ni	C/C_0	As	C/C_0 *
Western Coal	Alkaline	Water	[illegible]	[illegible]	<0.02	NA	<0.02	NA	0.9	NA	0.2	NA	<0.01	NA	0.01	NA		
		1	2.0	[illegible]	[illegible]	[illegible]	[illegible]	0.27	100	0.80	48	0.86	14.9	0.97	10.7	0.92	0.19	0.21
		2	0.75	4.8	62	0.38	6	0.008	33.4	0.75	120	0.60	7.4	1.00	1.27	0.90	0.02	
		3	0.40	4.2	80.4	0.002	2.9	0.048	12.3	0.47	18.0	0.18	2.80	0.91	1.38	0.67	<0.001	
		4	0.20	7.1	<0.02	0.001	0.06	0.004	1.3	0.08	0.7	0.01	0.18	0.21	0.02	0.07	<0.005	
Economizer Ash	Highly Alkaline	Water	3.0	12.2	<0.02	NA	<0.02	NA	0.7	NA	0.1	NA	<0.01	NA	0.04	NA		
		1	2.0	4.1	600	0.78	80	0.11	5.7	0.04	2.2	0.001	[illegible]	1.77	9.97	0.85	<0.024	
		2	1.0	11.9	<0.02		<0.02		17.0	0.26	[illegible]	0.01	<0.02		<0.02		0.016	0.01
		3	0.40	12.3	<0.02		<0.02		4.0	0.16	<0.2		<0.02		<0.02		0.007	0.05
		4	0.20	12.1	<0.02		<0.02		2.6	0.20	<0.2		<0.01		<0.02		0.008	0.10
Precipitator Ash	Highly Alkaline	Water	3.0	11.4	<0.02	NA	<0.02	NA	10.0	NA	1.2	NA	<0.01		0.02			
		1	2.0	4.1	4,210	0.90	50	0.28	128	1.00	88	0.68	25.4	1.52	11.7	1.00	0.14	0.15
		2	0.75	4.6	1198	0.75	3	0.35	3.3	0.02	0.8	0.004	9.9	1.79	1.40	0.85	0.001	0.06
		3	0.40	5.6	84.4	0.008	0		6.7	0.27	1.1	0.01	4.28	1.38	0.02	0.008	0.014	0.08
		4	0.20	11.7	<0.02		<0.02		2.3	0.17	<0.2		<0.01		<0.02		0.90	1.23
FGD Scrubber Sludge	Limestone Process	Water	3.0	8.0	<0.02	NA	<0.02	NA	2.2	NA	0.1	NA	0.02	NA*	0.02	NA		
		1	2.0	6.0	0.20	0.67	120	0.46	32.2	0.08	4.8	0.008	16.7	1.08	8.8	0.77	0.019	0.02
		2	0.40	6.6	2.8	0.274	4	0.077	4.5	0.19	<0.2		4.04	1.30	0.08	0.41	0.010	0.07
		3	0.20	7.1	17.8	0.008	0.6	0.008	4.5	1.48	<0.2		1.70	1.08	0.22	0.29	0.010	0.13
		4	0.08	7.8	<0.02		<0.02		5.8	1.54	<0.2		0.21	0.46	<0.02		0.024	0.92
Peat	50% Organic Content	Water	3.0	3.4	<0.02	NA	<0.02	NA	0.1	NA	0.1	NA	<0.01	NA	0.01	NA		
		1	2.0	4.1	1000	0.21	80	0.35	28	0.22	37	0.06	21.4	1.39	[illegible]	0.13	0.012	0.01
		2	0.75	4.6	108	0.008	2.0	0.022	2.4	0.05	1.3	0.008	8.6	1.00	0.12	0.02	0.008	0.02
		3	0.40	4.6	14.3	0.013	0		1.3	0.05	0.6	0.008	5.2	1.08	0.03	0.01	0.008	0.08
		4	0.25	4.8	0.2	0.004	[illegible]	0.019	1.1	0.08	0.2	0.001	2.24	1.40	<0.02		0.008	0.10
Bottom Ash	Alkaline	Water	3.0	8.0	<0.02	NA	<0.02	NA	0.2	NA	2.6	NA	<0.01	NA	0.01	NA		
		1	0.5	4.2	4210	0.90	80	0.35	111	0.87	41	0.94	16.6	1.08	9.8	0.84	0.30	0.31

*Element concentrations in μg/mℓ

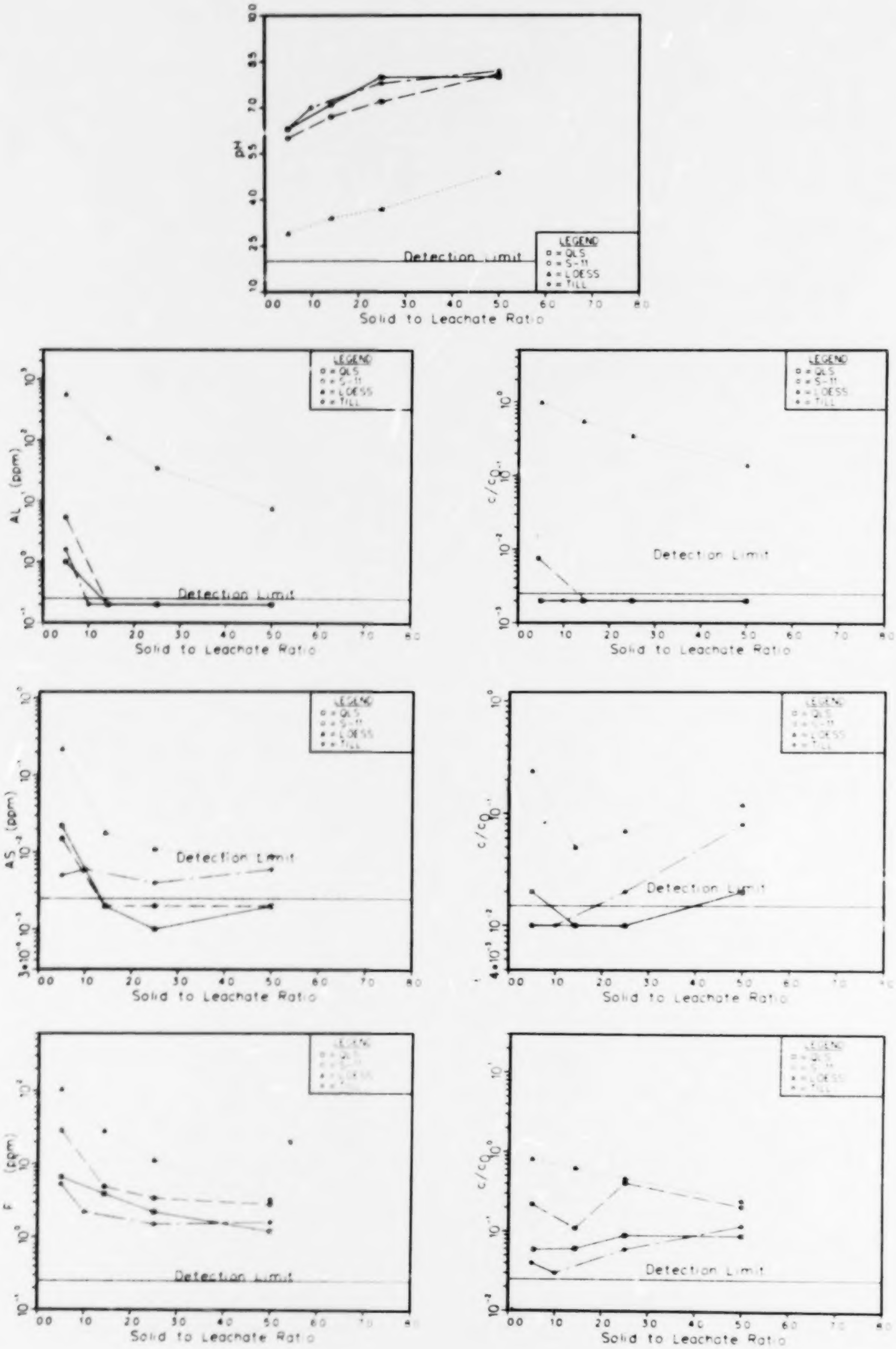

Fig. E-1.
Trace elements in effluents attenuated by sorbents.

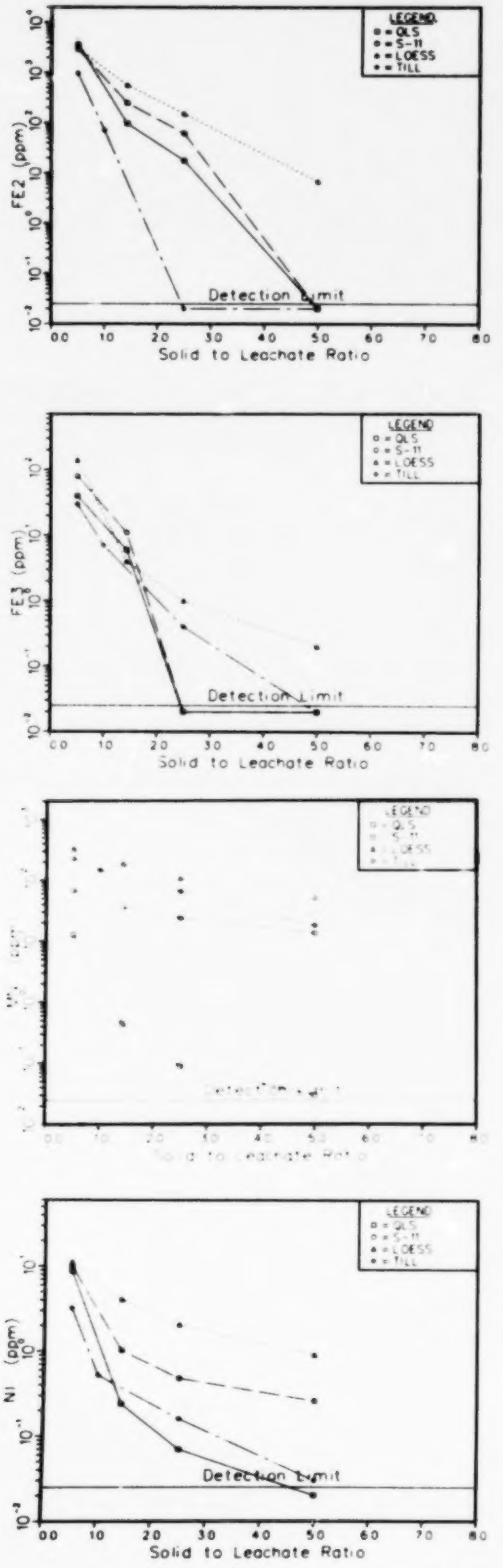

Fig. E-1 (contd).
Trace elements in effluents attenuated by sorbents.

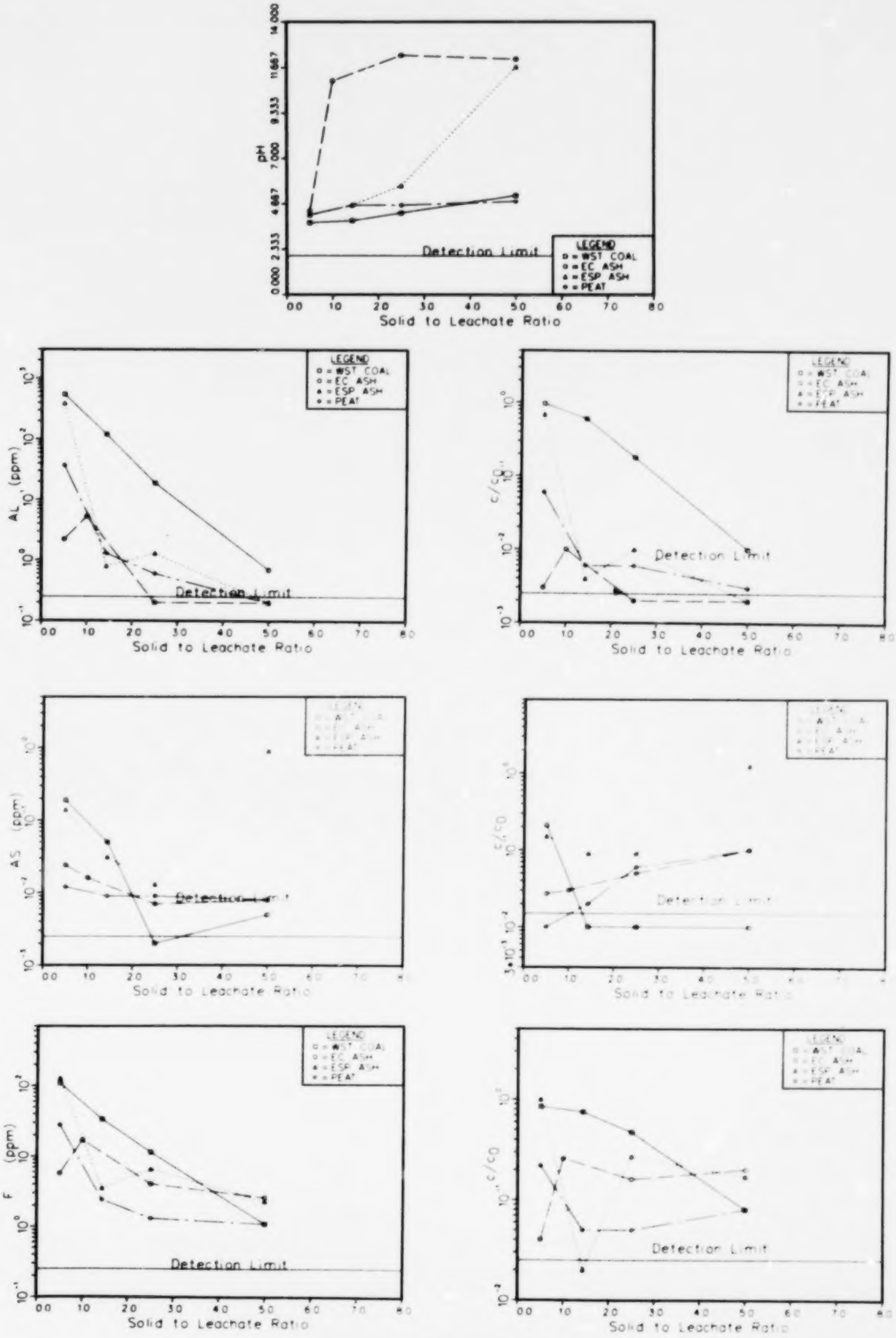

Fig. E-1 (contd).
Trace elements in effluents attenuated by sorbents.

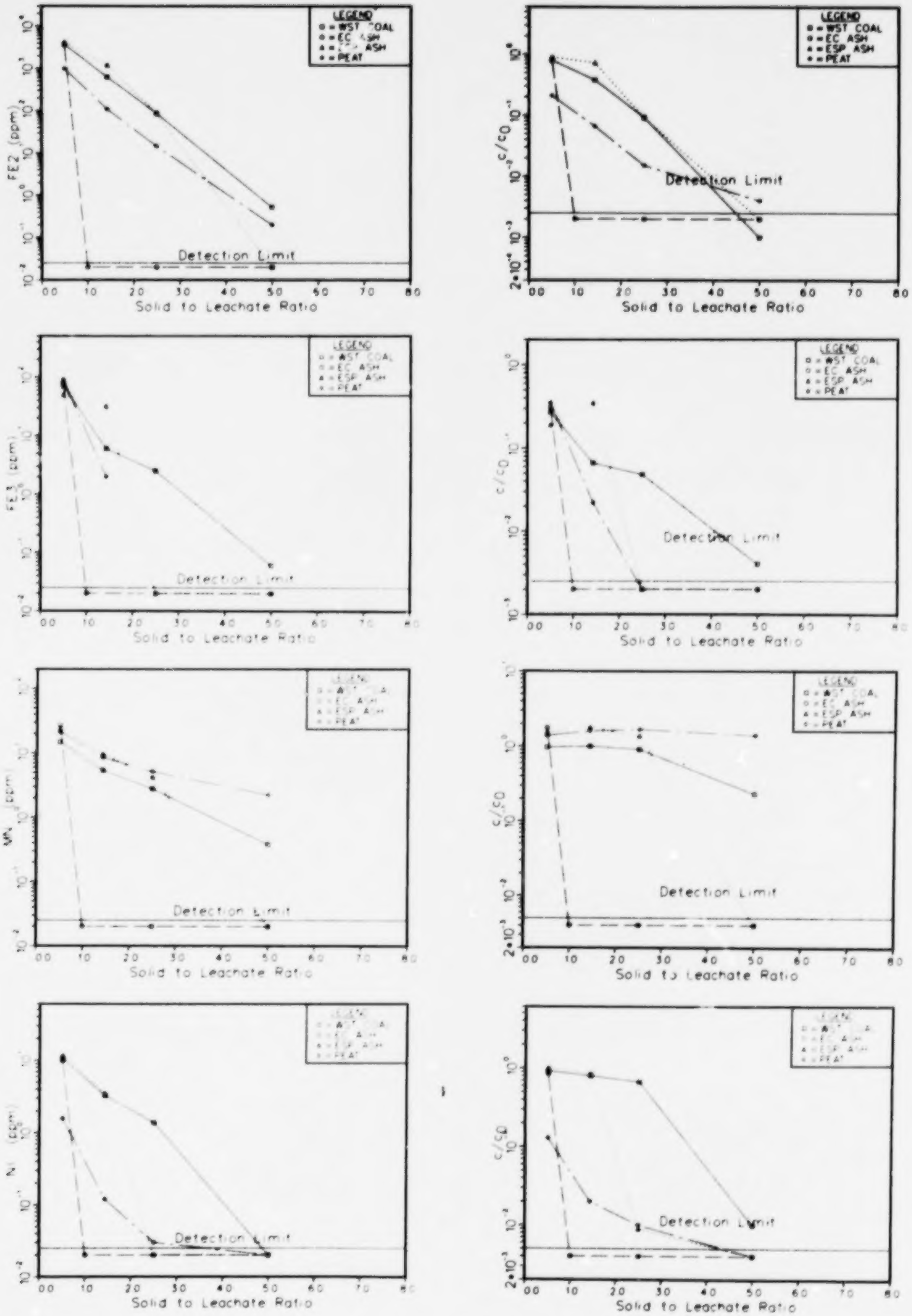

Fig. E-1 (contd).
Trace elements in effluents attenuated by sorbents.

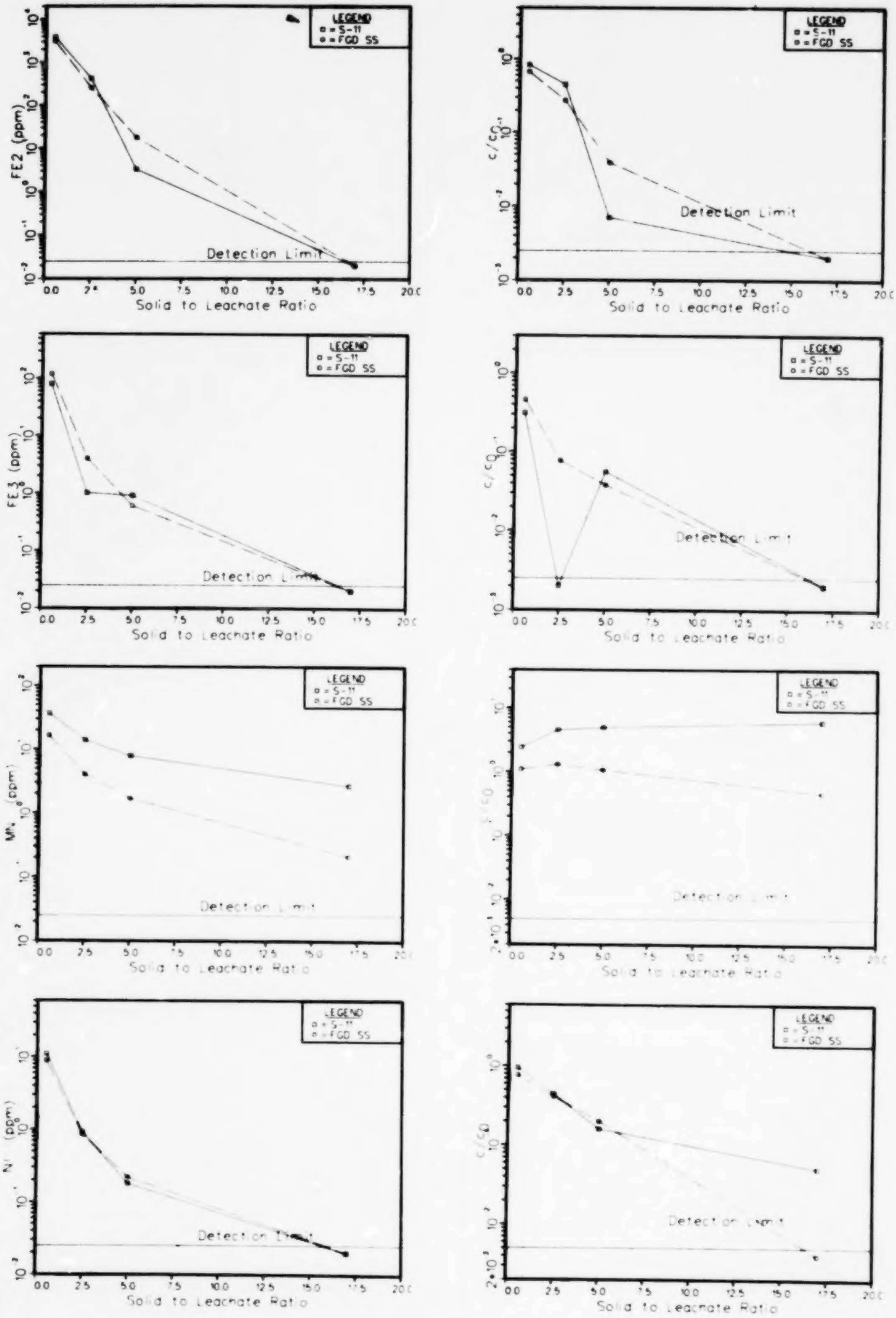

Fig. E-1 (contd).
Trace elements in effluents attenuated by sorbents.

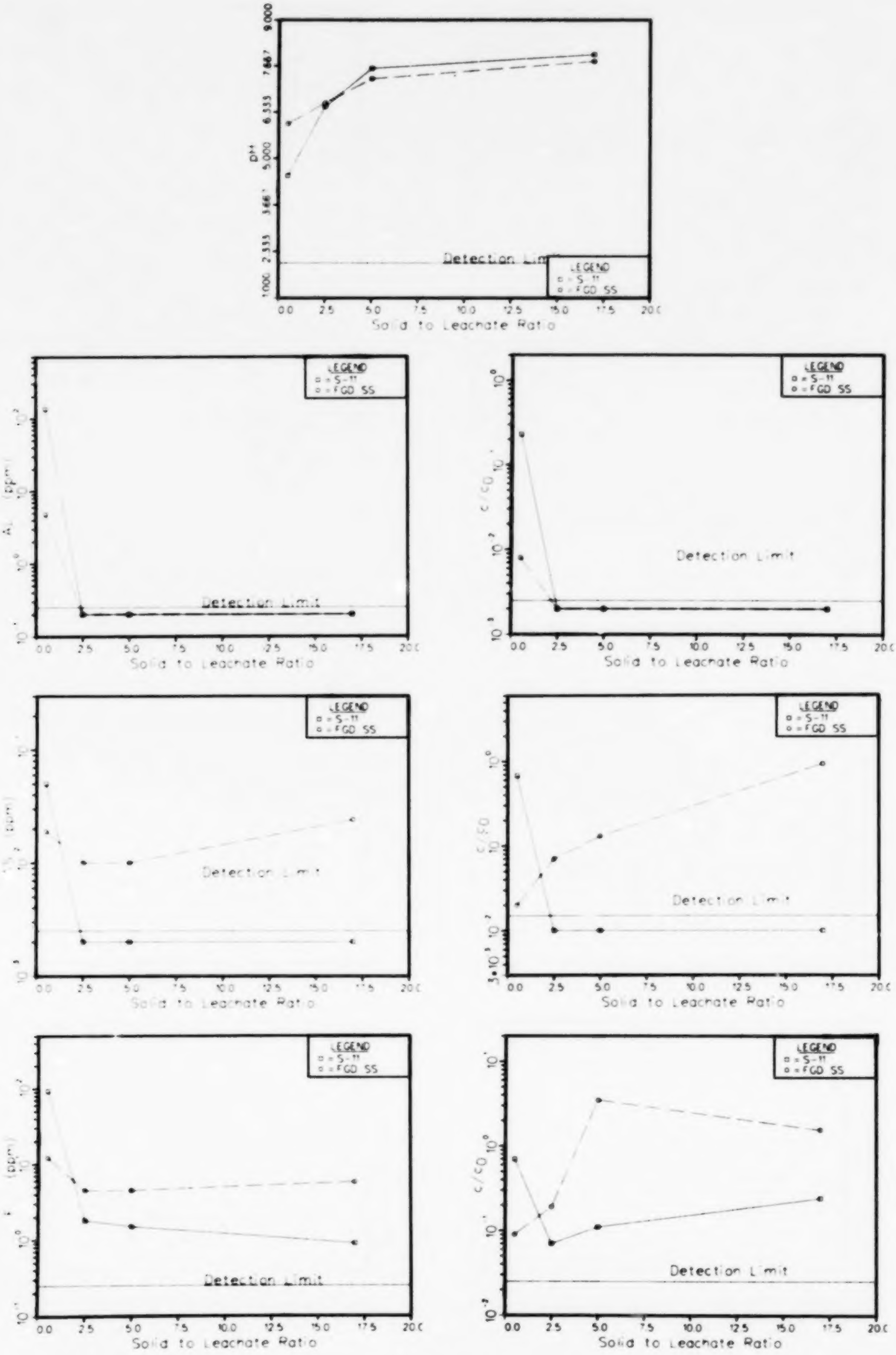

Fig. E-1 (contd).
Trace elements in effluents attenuated by sorbents.

APPENDIX F

EFFECT OF pH ON TRACE ELEMENT LEVELS IN COAL WASTE LEACHATES

Coal waste leachate CTWT-1012, which had been stored for many months under argon, was metered out (50 mℓ) into 125-mℓ Erlenmeyer flasks which were purged with argon and stoppered. Varying amounts of hydrated lime, $Ca(OH)_2$, were added to each flask to raise the pH. The flasks were purged with argon, resealed, and stirred with magnetic stirrers for 24 h. After equilibrating, the slurries were vacuum filtered under argon through 0.45-μm Millipore disks. The filtrates were tested for pH, Fe++ and Fe+++, and then acidified for further elemental analyses. These results are posted in Table F-I. Plots of most of the elements are given in Fig. 11 in the section on "Treating the Waste Effluent."

TABLE F-4

TRACE ELEMENT LEVELS AS A FUNCTION OF THE pH OF A COAL WASTE LEACH[a]

CTWT-17	LIME (g)[b]	pH	Al	As	Ca	Cd	Co	Cr	Cu	F	Fe	Fe^{++}	Fe^{+++}	Mn	Mo	Ni	Zn
0	–	2.25	370	.41	350	.21	3.5	.43	.09	81	3310	1680	1630	9.9	<.1	7.5	16
1	0.16	2.73	370	.14	540	.23	3.7	.28	.11	86	1960	1800	160	10.1	<.1	7.7	17
2	0.35	5.82	.46	<.01	430	.08	2.8	<.01	.01	2.0	1350	1350	<0.02	10.8	<.1	3.8	3
3	0.43	6.49	<.1	<.006	450	<.003	.5	<.01	<.01	4.2	620	620	<0.02	8.1	<.1	.5	.5
4	0.50	8.09	<.1	<.003	500	<.003	<.02	<.01	<.01	10.	2.2	2.2	<0.02	0.3	<.1	<.02	<.02
5	0.60	10.18	1.1	<.003	490	<.009	<.02	<.04	<.01	12.	<.02	<0.02	<0.02	<.02	<.4	<.02	<.02

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[a] CTWT-1012 leachate used; argon atmosphere throughout experiment.

[b] Grams of hydrated lime slurried in 25 mℓ water and added to 50 mℓ of leachate.

APPENDIX G

LIME/LIMESTONE/COAL WASTE SLURRIES - AN ATTRACTIVE ROUTE TO COAL WASTE DISPOSAL

I. PREPARING THE LIME/LIMESTONE/COAL WASTE SLURRIES

Three 55-gal. drums of Plant M, high-sulfur, Illinois-Basin coal preparation waste were crushed to minus 3/8 in. without prior drying. Scoops of material from each barrel were placed, in sequence, into six empty barrels fitted with plastic liners until 250 lbs of material were present in each barrel. To each barrel, 30 ℓ of deionized water were added and the barrel tumbled for 5 min at 15 rpm. After the barrels had stood for several days, the excess water (approximately 8 ℓ) was siphoned off and analyzed for acidity. The leachates had pH values from 2.8 to 2.9 and were 0.045 molar in acid. To each barrel was added a slurry (generally 38 to 50% solids) of lime. This slurry was blended into the waste slurry by tumbling the barrel at 15 rpm for 2 minutes. In one case, limestone was later added and blended. (Each mixture sat for 4 to 9 days as other barrels were being prepared and used.) After settling, excess water was siphoned off, and the slurry was poured into a muslin filter in a 90- by 150- by 25-cm polyethlyene tub and spread out evenly to allow further water drainage. The slurry was then ready for use. A listing of the lime and limestone levels and pH values for each slurry is given in Table G-I.

II. DUMPING THE SLURRIES INTO DISPOSAL BOXES

The drained lime/limestone/waste slurries were portioned out into several groups. The first six portions (1/10 barrel each) were placed in molded plastic pans which had previously been fitted with Tygon drains covered with glass wool that, in turn, was covered with sand (see Fig. 12c in the text). The plastic, scale-up boxes were then placed in a 6-column by 6-row grid for weathering by raining and drying cycles.

The remainder of each barrel was divided into numerous 600-g and 4000-g units. These portions were sealed in polyethylene bags from which the air had been excluded by rolling them up like toothpaste tubes before sealing. These portions have been sealed as wet, oxygen-deficient controls.

III. RAIN-DRY WEATHERING CYCLES (IN PROGRESS)

The weathering cycles start with Monday morning "rain showers" of 1650 mℓ of deionized water (equivalent of 39 in/yr), with the drains stoppered. On Tuesday the drains are opened and the leachates allowed to drain out. (This overnight soaking increases the water-to-waste contact.) These leachates are monitored weekly for pH, conductivity, volume of flow, and ferric and ferrous ion levels. (Results for the first 9 weeks are given in Tables G-II to G-IV.) Samples are retained for trace element levels, to be measured at a later time. The drained boxes of lime/limestone/waste are then allowed to dry until the next Monday, when the cycle is started again.

TABLE G-I

LIME/LIMESTONE/COAL WASTE SLURRIES[a]

Barrel #	Additive	Amount (g)	Level (%)[b]	Water(ℓ)[c]	pH[d]	
					Immediate[e]	Steeped (days)[f]
1	Lime[g]	192	0.17	20.5	6.3	5.6(9)
2	Lime	377	0.33[h]	20.6	11.0	6.5(9)
3	Lime	599	0.53	21.8	-	8.6(7)
4	Lime	1276	1.12	25.6	12.6	11.0(9)
5	Lime	3784	3.33	30.2	-	12.1(6)
6[i]	Lime +	314	0.35	21.0	-	7.6(4)
	$CaCO_3$[j]	982	1.08			

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[a] 113.5 kg (250 lb) waste/barrel.

[b] Based on waste.

[c] In final slurry.

[d] Slurry + extra deionized water; allowed to settle; electrode placed in liquid only.

[e] Immediately after lime slurry added and mixed.

[f] Slurries allowed to settle before siphoning off most of the excess water.

[g] -325 mesh hydrated lime.

[h] Amount of lime needed to neutralize acid in slurry exactly; based on base titration of hydrogen peroxide-treated leachate.

[i] Only 90.8 kg (200 lb) used.

[j] -80 mesh precipitated limestone.

TABLE G-II

pH OF EFFLUENTS FROM WEATHERED BOXES OF SLURRY-TREATED COAL WASTE[a]

Time	Lime (%)					Lime (%) Limestone
(weeks)	0.17	0.33	0.53	1.1	3.3	0.35 + 1
0	5.6	6.5	8.6	11.0	12.1	7.6
3	2.4	2.5	3.8	2.2	11.7	7.4
6	2.2	2.2	2.4	4.2	11.5	7.3
9	2.0	2.0	2.0	3.0	9.6	7.5
12	1.8	1.9	1.9	2.8	7.6	7.4

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[a] Values are pH units.

TABLE G-III

TOTAL IRON IN EFFLUENTS FROM WEATHERED BOXES OF SLURRY-TREATED COAL WASTE[a]

Time	Lime (%)					Lime (%) Limestone
(weeks)	0.17	0.33	0.53	1.1	3.3	0.35 + 1
3	3700	1600	3.9	1.4	0.3	<0.01
6	8500	10000	3600	0.8	<0.01	<0.01
9	14000	13000	14000	3.9	0.1-0.3	0.01
12	12000	10000	23000	4-50	0.1-0.9	0.05

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[a] Values in ppm.

TABLE G-IV

CONDUCTIVITY OF EFFLUENTS FROM WEATHERED BOXES OF SLURRY-TREATED COAL WASTE[a]

Time (weeks)	Lime (%) 0.17	0.33	0.53	1.1	3.3	Lime (%) Limestone 0.35 + 1
3	4.4	3.3	1.2	5.1	2.7	1.3
6	6.3	5.9	4.4	1.3	1.6	1.2
9	8.5	7.9	8.3	1.5	1.4	1.1
12	10.6	10.1	10.6	3.0	1.4	1.2

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[a] Values in grams KCl per liter equivalents.

IV. DISPOSAL BOX DISMANTLEMENT AND SOLID WASTE EVALUATION (IN PROGRESS)

Plans also call for dismantling a box from each lime/limestone/waste level at various times to permit an evaluation of the depth of degradation The scheduled periods are 1 week, 1 month, 3 months, 6 months, 1 year, and 2 years. Each dismantled box will produce one fraction in which 2.5 cm is skimmed off half of the top and another in which a vertical third of the layer between this and the sand layer is removed. These fractions will be sealed in polyethylene bags for later analyses. The boxes for the first week have been spread out and allowed to dry. At various times, fractions from these will be separated and "rained" upon. This will provide an evaluation of the influence of air oxidation in the absence of rain water.

APPENDIX H

TRACE ELEMENT AND MINERAL ANALYSES AND CORRELATIONS FOR A LOW-SULFUR APPALACHIAN COAL PREPARATION PLANT

Procedures for sizing are discussed in the first annual report (LA-6835-PR). Float/sink procedures are described in the second annual report (LA-7360-PR). Statistical correlation treatment is discussed in the section on "Visual Presentation of Statistical Results" in this report. Tables H-I through H-IV and Figs. H-1 and H-2 give specific data on waste from Plant G coal preparation.

TABLE H-I

SUMMARY OF PLANT G COAL AND REFUSE SAMPLES

Identity	Sample	Wt (kg)	% of Whole
Feed Coal A	38	47	100
Feed Coal B	39	45	100
Coarse Gob A	40	60	100
Coarse Gob B	41	61	100
Fine Gob	42	43	100
Average Gob: Sized	40A		100
-20 mesh	40G		8.9
<1/4 in.	40B		27.5
<1 in.	40C		31.5
<1 in(1D)	40E		7.9
<2 in.	40E		7.2
>2 in.	40F		17.0
Average Gob: Float/Sink	40A		100
Float < 2.15g/ml	F18F		31.0
Float < 2.48, Sink > 2.15	F18E		31.0
Float < 2.97, Sink > 2.48	F18C		37.7
Sink > 2.97	F18A		0.3

TABLE H-II

TRACE ELEMENT AND MINERAL CONTENT OF COAL WASTE MATERIALS FOR APPALACHIAN PLANT G SAMPLES

SAMPLE	38	39	40	41	42
IDENTITY (1)	FED COAL A	FED COAL B	GOB A CONS	GOB B CONS	FN GOB
LOCALE	PLANT G	PLANT G	PLANT G	PLANT G	PLANT G
DATE OBTND	06/23/76	06/23/76	06/23/76	06/23/76	06/23/76
PCT H2O	5.49	5.41	4.54	4.60	20.14
PCT LTA	46.78	40.45	84.82	81.52	78.35
PCT ORIGNL	100.00	100.00	100.00	100.00	100.00
SIZE,KG	46.30	44.60	59.70	60.80	42.60
CHNS ANAL					
NITROGEN	.68	.66	.26	.42	.46
SULFUR	.72	.69	.60	.64	.68
MINERALOGY					
KAOLINITE			11.18	11.34	11.16
ILLITE			19.03	19.61	19.46
QUARTZ			23.87	19.76	21.31
PYRITE			-1.00	-1.00	-1.00
CALCITE			1.03	.49	1.92
MIXED CLAY			7.47	3.49	6.29
GYPSUM			1.52	1.58	.76

SAMPLE	38	39	40	41	42
ELEMENT (2)	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS
LI PPM H A	61.00	61.00	119.00	132.00	114.00
BE PPM H A	2.20	2.70	3.00	2.60	1.60
B PPM L E	52.00	46.00	56.00	56.00	52.00
F PPM	340.00	300.00	600.00	560.00	550.00
NA PCT H A	.06	.05	.17	.11	.12
MG PCT H A	.27	.23	.52	.57	.52
AL PCT H A	5.08	4.26	9.56	9.25	8.88
SI PCT R O	10.24	9.58	20.20	20.45	20.10
P PPM R O	40.00	90.00	160.00	150.00	150.00
CL PPM R N	329.00	305.00			
K PCT H A	.49	.83	2.07	2.05	1.99
CA PCT H A	.13	.10	.12	.15	.14
SC PPM R N	8.83	8.94	15.80	17.20	14.60
TI PCT R N	.34	.36	.73	.67	.56
V PPM R N	75.20	67.10	116.00	116.00	109.00
CR PPM H A	58.00	47.00	87.00	104.00	86.00
MN PPM H A	51.15	42.10	93.90	96.75	99.50
FE PCT H A	1.07	.93	1.89	2.05	2.10
CO PPM R N	13.00	12.00	9.00	11.00	14.00
NI PPM L E	32.00	33.00	55.00	46.00	45.00
CU PPM H A	30.00	31.00	43.00	53.00	47.00
ZN PPM H A	43.00	38.00	72.00	69.00	65.00
GA PPM L E	8.90	10.90	22.20	19.30	17.00
GE PPM L E	-5.00	-4.00	-8.00	-8.00	-8.00
AS PPM R N	8.15	5.99	14.20	20.30	16.60
RB PPM R N	126.00	63.50	121.00	134.00	141.00
Y PPM L E	15.00	12.00	21.00	19.00	16.00
ZR PPM L E	69.00	78.00	160.00	130.00	99.00
MO PPM L E	-5.00	-4.00	-8.00	-8.00	-8.00
CD PPM H A	.20	.10	.20	.40	.40
SN PPM L E	-5.00	-4.00	-8.00	-8.00	-8.00
SB PPM R N	1.00	1.07		2.95	1.52
CS PPM R N	3.99	4.46	9.22	9.58	7.52
LA PPM R N	27.50	23.90	58.30	52.40	38.00
CE PPM R N	41.10	40.40	74.50	55.80	76.50
SM PPM R N	2.10	2.97	6.09	5.50	4.34
EU PPM R N	.60	.54	1.13	1.50	1.14
TB PPM R N			.80	1.56	.94
DY PPM R N	2.64	3.66	5.82	5.68	5.18
YB PPM R N		1.68	2.83	2.46	3.00
LU PPM R N	.23	.21	.59	.56	.13
HF PPM R N	2.05	2.88	5.73	4.02	4.76
TA PPM R N			1.46	1.14	.78
W PPM R N					1.32
PB PPM H A	21.00	15.00	22.00	20.00	27.00
TH PPM R N	7.19	9.13	15.60	15.80	13.90
U PPM R O	2.71	2.55	4.32	4.40	3.84

TABLE H-III

TRACE ELEMENT CONTENT OF SIZED WASTE MATERIALS FOR APPALACHIAN PLANT G SAMPLES

SAMPLE	40A	40B	40C	40D	40E	40F
IDENTITY (1)	-20	-1/4	-1	-1D	-2	+2
LOCALE	PLANT G	PLANT G	PLANT G	PLANT G	PLANT G	PLANT G
DATE OBTND	06/23/76	06/23/76	06/23/76	06/23/76	06/23/76	06/23/76
PCT LTA	87.53	82.59	83.69	35.62	81.27	66.95
PCT ORIGNL	8.89	27.49	31.51	7.87	7.22	17.03

CHMS ANAL

NITROGEN	.45	.42	.36	.36	.45	[illegible]
SULFUR	1.22	.62	.57	.42	.31	.66

SAMPLE ELEMENT (2)	40A RAW BASIS	40B RAW BASIS	40C RAW BASIS	40D RAW BASIS	40E RAW BASIS	40F RAW BASIS
LI PPM H A	110.00	121.00	123.00	130.00	142.00	117.00
BE PPM H A	2.50	2.60	2.70	3.20	2.20	2.20
B PPM L E	52.00	56.00	54.00	64.00	54.00	56.00
F PPM H O	540.00	600.00	590.00	640.00	560.00	620.00
NA PCT H A	.12	.17	.12	.13	.12	.13
MG PCT H A	.49	.59	.58	.66	.54	.60
AL PCT H A	8.43	9.10	10.02	10.23	9.43	9.44
SI PCT H O	18.14	19.66	19.50	20.20	16.61	21.65
P PPM H O	140.00	150.00	140.00	170.00	150.00	160.00
CL PPM N N	82.90	96.40				
K PCT H A	1.87	2.15	2.08	2.31	2.00	2.17
CA PCT H A	.63	.14	.16	.16	.22	.11
SC PPM H N	15.60	16.20	17.20	17.10	19.20	16.90
TI PCT H N	.56	.60	.68	.64	.72	.69
V PPM H N	110.00	124.00	122.00	124.00	127.00	119.00
CR PPM H A	63.00	84.00	92.00	86.00	95.00	63.00
MN PPM H A	90.60	105.00	101.00	110.50	81.55	128.00
FE PCT H A	2.34	2.14	1.92	2.01	1.47	2.22
CO PPM H N	9.00	9.00	7.00	11.00	13.00	15.00
NI PPM L E	42.00	58.00	52.00	56.00	56.00	52.00
CU PPM H A	65.00	42.00	39.00	51.00	54.00	51.00
ZN PPM H A	71.00	87.00	79.00	62.00	67.00	62.00
GA PPM H N	21.60	19.70	21.90	21.10	21.10	21.50
GE PPM L E	-9.00	-8.00	-8.00	-9.00	-8.00	-9.00
AS PPM H N	20.40	14.10	12.40	7.36	5.44	15.60
RB PPM H N	97.00	109.00	134.00	174.00	136.00	16[illegible].00
Y PPM L E	22.00	22.00	19.00	21.00	21.00	23.00
ZR PPM L E	170.00	170.00	130.00	160.00	190.00	160.00
MO PPM L E	-9.00	-8.00	-8.00	-9.00	-8.00	-9.00
CD PPM H A	.40	.40	.20	.20	.90	.40
SN PPM L E	-9.00	-8.00	-8.00	-9.00	-8.00	-9.00
SB PPM H N	1.70		2.40			.54
CS PPM H N	7.32	10.10	7.62	9.61	11.20	8.05
LA PPM H N	43.00	40.30	52.[illegible]	32.10	55.00	59.40
CE PPM H N	31.00	62.60	92.50	[illegible].30	45.00	94.00
SM PPM H N	3.76	4.76	6.29	5.28	5.49	[illegible].17
EU PPM H N	1.33	1.23	1.44	1.53	1.50	1.00
TB PPM H N			1.35	1.12	1.32	
[illegible]	4.45	4.77	5.27	[illegible]	[illegible]	[illegible]
[illegible]	3.42	2.40	[illegible]	[illegible]	2.0[illegible]	[illegible]
LU PPM H N	.49	.5[illegible]	.[illegible]	.5[illegible]	.4[illegible]	.[illegible]
HF PPM H N	4.15	[illegible]	.[illegible]	5.[illegible]7	[illegible].73	6.42
TA PPM H N	.80	.44	1.2[illegible]	[illegible].32	1.0[illegible]	1.37
W PPM H N			.34	4.76		
PB PPM H A	43.00	1[illegible].00	24.00	2[illegible].00	25.00	20.00
TH PPM H O	14.10	14.70	15.70	15.60	1[illegible].40	16.40
U PPM H O	3.82	3.86	4.23	4.80	4.54	[illegible].05

TABLE H-IV

TRACE ELEMENT CONTENT OF FLOAT/SINK-SEPARATED WASTE FROM APPALACHIAN PLANT G

SAMPLE	F18A	F18C	F18E	F18F
IDENTITY (1)	40A SK/1PE	40A SK/DBM	40A SK/DBE	40A F/DBE
LOCALE	PLANT G	PLANT G	PLANT G	PLANT G
PCT ORIGNL	.32	37.73	30.90	31.04
CHNS ANAL				
NITROGEN		.14	.28	.70
SULFUR	35.70	.26	.56	.65

SAMPLE	F18A	F18C	F18E	F18F
ELEMENT (2)	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS
LI PPM R A	11.40	125.00	133.00	94.00
BE PPM R A	-10.00	3.10	3.30	2.50
B PPM L E	94.00	95.00	70.00	41.00
F PPM R O		300.00	680.00	320.00
NA PCT H A	.03	.18	.14	.06
MG PCT H A	.14	.78	.52	.22
AL PCT H A	1.43	11.21	10.06	5.50
SI PCT H O	2.68	23.94	21.18	10.61
P PPM H O		190.00	150.00	100.00
CL PPM R O	62.00	60.00	250.00	160.00
K PCT H A	.29	2.76	2.08	.90
CA PCT H A	[illegible]	.16	.37	.02
SC PPM R N	4.20	19.70	17.50	11.60
TI PCT R N	.44	.67	.66	.33
V PPM R N	140.00	130.00	120.00	220.00
CR PPM R A	88.00	91.00	100.00	74.00
MN PPM H A	370.00	159.00	93.50	30.00
FE PCT H A	31.10	2.47	1.83	.86
CO PPM R N	16.00	12.20	13.80	16.00
NI PPM L E	50.00	24.00	52.00	35.00
CU PPM H A	270.00	39.00	44.00	59.00
ZN PPM H A	240.00	65.00	126.00	37.00
GA PPM R N	-.50	27.00	30.70	-.50
GE PPM L E	-30.00	-30.00	-30.00	-20.00
AS PPM R N	1200.00	14.30	15.60	-1.00
BR PPM R N	-20.00	230.00	188.00	45.90
Y PPM L E	29.00	27.00	26.00	21.00
ZR PPM L E	750.00	200.00	220.00	160.00
MO PPM L E	50.00	-10.00	-9.00	-7.00
CD PPM R A	-100.00	.40	.50	.30
SN PPM L E	-10.00	-10.00	-9.00	-7.00
SB PPM R N	5.73	-1.00	-1.00	-1.00
CS PPM R N	2.10	5.84	6.74	4.67
LA PPM R N	2610.00	46.40	51.00	30.90
CE PPM R N	67.10	121.00	104.00	44.40
SM PPM R N	4.2[illegible]	8.09	6.25	4.50
EU PPM R N	1.21	1.47	1.23	.60
TB PPM R N	.42	.67	.65	-.10
DY PPM R N	2.60	4.50	2.90	.62
YB PPM R N	3.43	3.86	2.90	.37
LU PPM R N	.32	.54	.49	.12
HF PPM R N	17.50	4.57	4.26	2.32
PB PPM H A	160.00	22.00	34.00	39.00
TH PPM R O	5.04	18.10	17.10	1.15

FOOTNOTES

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(1) PLUS OR MINUS INDICATES SIZE GREATER OR LESS THAN SIZE GIVEN. NUMBERS 6 OR LARGER ARE MESH SIZES, OTHERS ARE IN INCHES

(2) LETTERS INDICATE HOW SAMPLE WAS PREPARED AND ANALYZED

R= RAW SAMPLE
L= LOW TEMPERATURE ASH
H= HIGH TEMPERATURE ASH
N= NEUTRON ACTIVATION ANALYSIS
A= ATOMIC ABSORPTION
E= EMISSION SPECTROSCOPY
O= OTHER

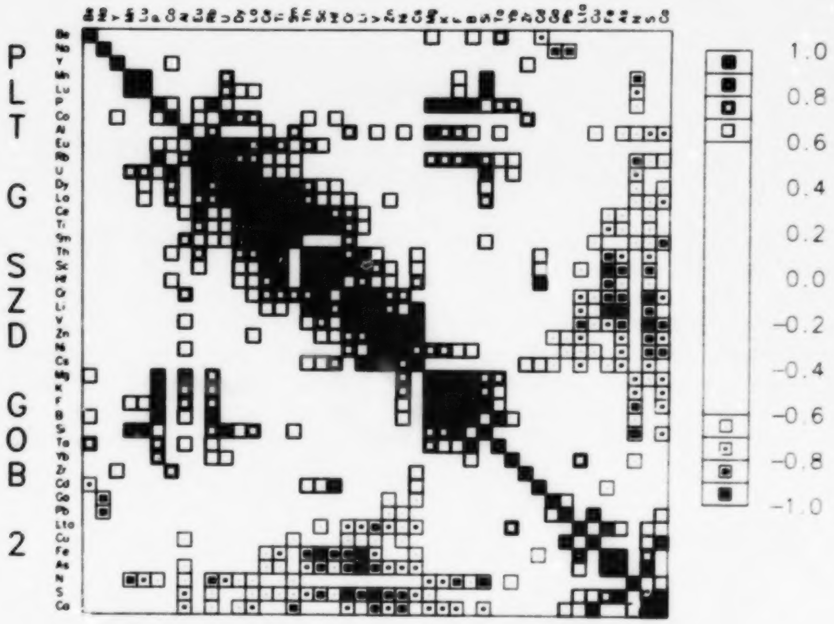

Fig. H-1.
Trace-element, correlation-coefficient clusters for sized fractions of the average coal preparation waste from Plant G.

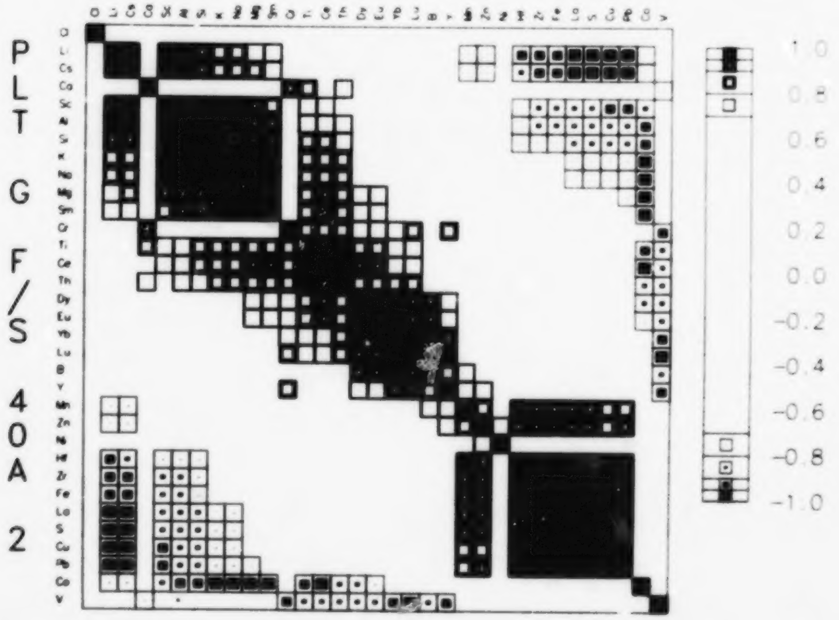

Fig. H-2.
Trace-element, correlation-coefficient clusters for float/sink fractions of the average coal preparation waste from Plant G.

APPENDIX I

BATCH LEACHINGS OF LOW-SULFUR, APPALACHIAN COAL PREPARATION WASTE FROM PLANT G

The experimental procedures for these leachings are those reported in Appendix H of the second annual report (LA-7360-PR, p. 116). The waste samples leached were composites of the originally collected, coarse waste samples reported in Appendix H that had been ground to less than 20 mesh. The leachings of 50 g waste with 250 mℓ of water were conducted at room temperature with the system open to the air. Shaking was performed with ninety 3-1/2-in. strokes/min. The element levels in the leachates are reported in Table I-I below. Ecology discharge severity is given in Table I-II.

TABLE I-I
TRACE ELEMENT LEVELS FROM THE BATCH LEACHINGS OF LOW-SULFUR, PLANT G COAL WASTE[a]

Sample No.	1	2	3	4	5
Time (Days)	0.01	1	4	16	42
pH	3.9	4.3	4.3	4.1	3.0
TDS (%)	0.10	0.13	0.09	0.10	0.23
F	1.4	2.0	2.3	2.6	3.1
Na	18	20	29	25	29
Mg	240	250	270	260	320
Al	29	25	28	40	280
K	90	130	135	170	165
Ca	580	810	850	840	960
Cr (μg/kg)	49	7	9	7	300
Mn	6	7	8	8	12
Fe	15	16	16	11	31
Co	1.5	1.5	2	2	3
Ni	3	4	4	5	6
Cu	3	1	1	2	6
Zn	4	5	6	7	15
Cd (μg/kg)	30	31	27	46	25

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[a] Values in μg/g unless otherwise noted.

TABLE I-II

DISCHARGE SEVERITY OF BATCH LEACHATES FROM LOW-SULFUR AND HIGH-SULFUR COAL WASTES[a]

	Plant			
Element	**G[b]**	**A[c]**	**C[d]**	**B[e]**
Ni	4	7	10	30
Mn	0.7	2	2	3
Fe	0.6	<0.004	70	400
Zn	0.5	0.06	0.7	5
Ca	0.5	2	0.9	0.5
Cd	0.3	0.07	1	2
Al	0.2	0.01	1	10
Cu	0.2	<0.02	0.01	0.3
Co	0.06	0.1	0.4	0.8
K	0.06	0.02	0.04	0.004
Cr	0.0003	0.0002	0.006	0.03

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[a] Based on μg of element leached per gram of waste in one day.

[b] One day batch values in this Appendix.

[c] GL-22-1.

[d] SGL-5-6.

[e] GL-21-1.

APPENDIX J

COLUMN LEACHINGS OF LOW-SULFUR APPALACHIAN COAL PREPARATION WASTE FROM PLANT G

Experiment procedures are given in Appendix I of the second annual report (LA-7360-PR, p. 117). Composite material of the coarse waste collected from the plant was crushed to less than 3/8 in., and 500 g was used in each of four columns, 4.6-cm I.D. Upward flow of water was at 0.5 mℓ/min.

For two samples (GL-23 and GL-24), the flow of water was stopped after approximately 3 ℓ had passed through, and the columns were drained and aired. Intermittently, these aired columns were moistened during a 2-wk period to simulate the wet and dry periods encountered by a refuse pile. At the end of the 2-wk period water flow was resumed as before until a total of 10 ℓ of water had passed through the column.

Element levels, pH, and total dissolved solids at various eluent volumes are given in Tables J-I to J-IV. Plots of these values are given in Fig. J-I. Ecology discharge severity is given in Table J-V.

TABLE J-I

COMPOSITION OF LEACHATE FROM A COLUMN LEACHING OF PLANT G COAL WASTE (GL-23)[a]

Sample No.	1	2	5	7	11	16	20	21[b]	22	24	27	32
Vol (ℓ)	0.092	0.177	0.435	0.789	1.445	2.489	3.403	3.746	3.829	4.017	4.853	5.815
pH	2.9	3.0	3.1	3.2	3.5	3.8	3.9	3.5	3.5	3.6	3.9	3.9
TDS (%)	0.47	0.45	0.28	0.14	0.06	0.02	0.01	0.06	0.04	0.01	<0.01	0.01
F	1.6	1.5	0.8	0.4	0.2	0.13	0.11	0.20	0.19	0.13	0.11	0.11
Na	16	14	6.3	2.4	1	0.7	0.7	3.7	2.9	1.7	0.6	0.5
Mg	260	230	140	61	16	3.3	1.7	16	12	5.6	1.6	1.1
Al	83	73	32	13	2.5	3	2	<0.5	<0.5	0.5	<0.5	<0.5
K	28	26	18	13	8	4	4	19	11	8	4	3
Ca	410	390	300	170	70	18	9	74	58	24	7	5
Cr (μg/ℓ)	100	96	34	13	5	4	1	1	1	1	1	1
Mn	9	8	4	2	0.5	0.1	0.07	0.4	0.4	0.2	0.05	<0.05
Fe	49	44	23	10	3.6	0.9	0.1	0.9	0.6	0.4	0.3	<0.1
Co	2	2	0.8	0.4	0.15	<0.05	<0.05	0.25	0.2	<0.05	0.06	<0.05
Ni	4	3	2	0.8	0.3	<0.06	<0.06	0.4	0.3	0.1	<0.06	<0.06
Cu	5	4	2	0.9	0.3	0.2	<0.1	0.6	0.3	0.2	<0.1	<0.1
Zn	7	6	4	2	0.5	0.1	0.08	0.9	0.7	0.3	0.08	0.05
Cd (μg/ℓ)	41	27	16	7	2.5	1.6	0.7	2.4	3.0	1	0.4	0.3

---

[a] Values in μg/mℓ unless otherwise noted.

[b] After column "air-regenerated"

TABLE J-II

COMPOSITION OF LEACHATE FROM A COLUMN LEACHING OF PLANT G COAL WASTE (GL-24)[a]

Sample No.	1	4	7	9	11	15	18	19[b]	21	23	26	30	31
Vol (ℓ)	0.208	0.450	0.784	1.081	1.483	2.483	3.127	3.443	3.610	4.035	4.675	5.393	7.065
pH	3.0	3.2	3.4	3.4	3.5	3.8	3.9	3.2	3.4	3.6	3.8	3.8	3.9
TDS (%)	0.43	0.20	0.10	0.07	0.03	<0.01	0.01	0.02	0.02	<0.01	<0.01	<0.01	<0.01
F	1.1	0.6	0.33	0.24	0.15	0.06	0.06	0.11	0.11	0.10	0.07	0.06	0.05
Na	14	5.8	2.5	1.7	1.0	0.7	0.7	2.3	2.1	1.1	0.7	0.6	0.6
Mg	220	110	53	34	19	3.2	1.7	11	11	3.9	1.6	1.3	1.1
Al	68	24	10	6	2	1	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
K	25	18	12	11	7	5	4	9	9	6	5	4	3
Ca	380	240	160	120	62	20	10	38	40	16	7	5	4
Cr (μg/ℓ)	92	22	9	4	4	3	4	5	3	<1	1.6	1.9	<1
Mn	8	3	1	0.8	0.4	0.1	0.05	0.3	0.3	0.1	<0.05	<0.05	<0.05
Fe	45	18	9	7	4	0.9	0.5	1	1	0.3	0.3	0.2	0.1
Co	1.5	0.7	0.4	0.3	0.15	<0.05	<0.05	0.15	0.15	0.05	<0.05	<0.05	<0.05
Ni	3	2	0.7	0.5	0.3	0.07	<0.06	0.3	0.3	0.1	<0.06	<0.06	<0.06
Cu	4	2	0.8	0.5	0.3	<0.1	<0.1	0.3	0.3	0.1	<0.1	<0.1	<0.1
Zn	6	3	1	1	0.4	0.1	0.09	0.4	0.5	0.2	0.1	0.09	0.08
Cd (μg/ℓ)	21	8	6	5	2	0.5	0.1	2	2	0.8	0.5	0.8	0.7

---

[a] Values in μg/mℓ unless otherwise noted.

[b] After column "air-regenerated".

TABLE J-III

COMPOSITION OF LEACHATE FROM A COLUMN LEACHING OF PLANT G COAL WASTE (GL-25)[a]

Sample No.	1	2	5	6	8	14	20	24
Vol (ℓ)	0.239	0.320	0.570	0.869	1.334	2.395	3.466	6.039
pH	2.9	3.0	3.1	3.2	3.5	3.7	3.9	4.0
TDS (%)	0.49	0.33	0.19	0.09	0.03	<0.01	<0.01	<0.01
F	1.3	1.0	0.6	0.4	0.1	0.08	0.06	0.06
Na	15	8.6	4.1	2.0	1.0	0.9	0.7	0.7
Mg	240	150	91	44	15	3.6	1.6	1.1
Al	100	62	25	11	3	<0.6	<0.5	<0.5
K	26	20	16	12	8	5	4	3
Ca	230	190	140	84	42	12	6	4
Cr (μg/ℓ)	110	80	30	12	2	0.8	0.6	1.1
Mn	9	5	3	1	0.5	0.1	<0.05	0.08
Fe	59	37	18	10	4.3	1.2	0.6	0.7
Co	2	1	0.6	0.3	0.2	<0.05	<0.05	<0.05
Ni	4	2	1	0.6	0.25	0.06	<0.06	<0.06
Cu	5	3	2	0.7	0.3	0.1	<0.1	<0.1
Zn	7	5	2	1	0.5	0.15	0.09	0.06
Cd (μg/ℓ)	30	19	9	5	2	1	0.5	0.3

---

[a] Values in μg/mℓ unless otherwise noted.

TABLE J-IV

COMPOSITION OF LEACHATE FROM A COLUMN LEACHING OF PLANT G COAL WASTE (GL-26)[a]

Sample No.	1	2	6	8	14	19	23
Vol (ℓ)	0.086	0.174	0.827	1.393	2.471	3.499	6.085
pH	2.9	3.0	3.3	3.5	3.8	3.9	4.0
TDS (%)	0.56	0.44	0.08	0.02	<0.01	<0.01	<0.01
F	1.6	1.1	0.2	0.1	0.06	0.06	0.06
Na	19	15	1.7	0.8	0.7	0.7	0.7
Mg	270	210	35	11	2.9	1.6	0.8
Al	120	87	8	1.6	<0.5	<0.5	<0.5
K	25	23	10	7	4	4	3
Ca	250	220	74	38	12	7	3
Cr (μg/ℓ)	170	100	6	0.5	<0.5	0.4	0.9
Mn	14	9	1	0.3	0.06	<0.05	<0.05
Fe	52	40	6.7	3	1	0.6	0.4
Co	2	2	0.2	0.07	<0.05	<0.05	<0.05
Ni	4	3	0.5	0.2	<0.06	<0.06	<0.06
Cu	5	4	0.6	0.2	<0.1	<0.1	<0.1
Zn	9	7	1	0.4	0.1	0.1	0.05
Cd (μg/ℓ)	40	32	11	2	0.5	0.4	0.3

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[a] Values in μg/mℓ unless otherwise noted.

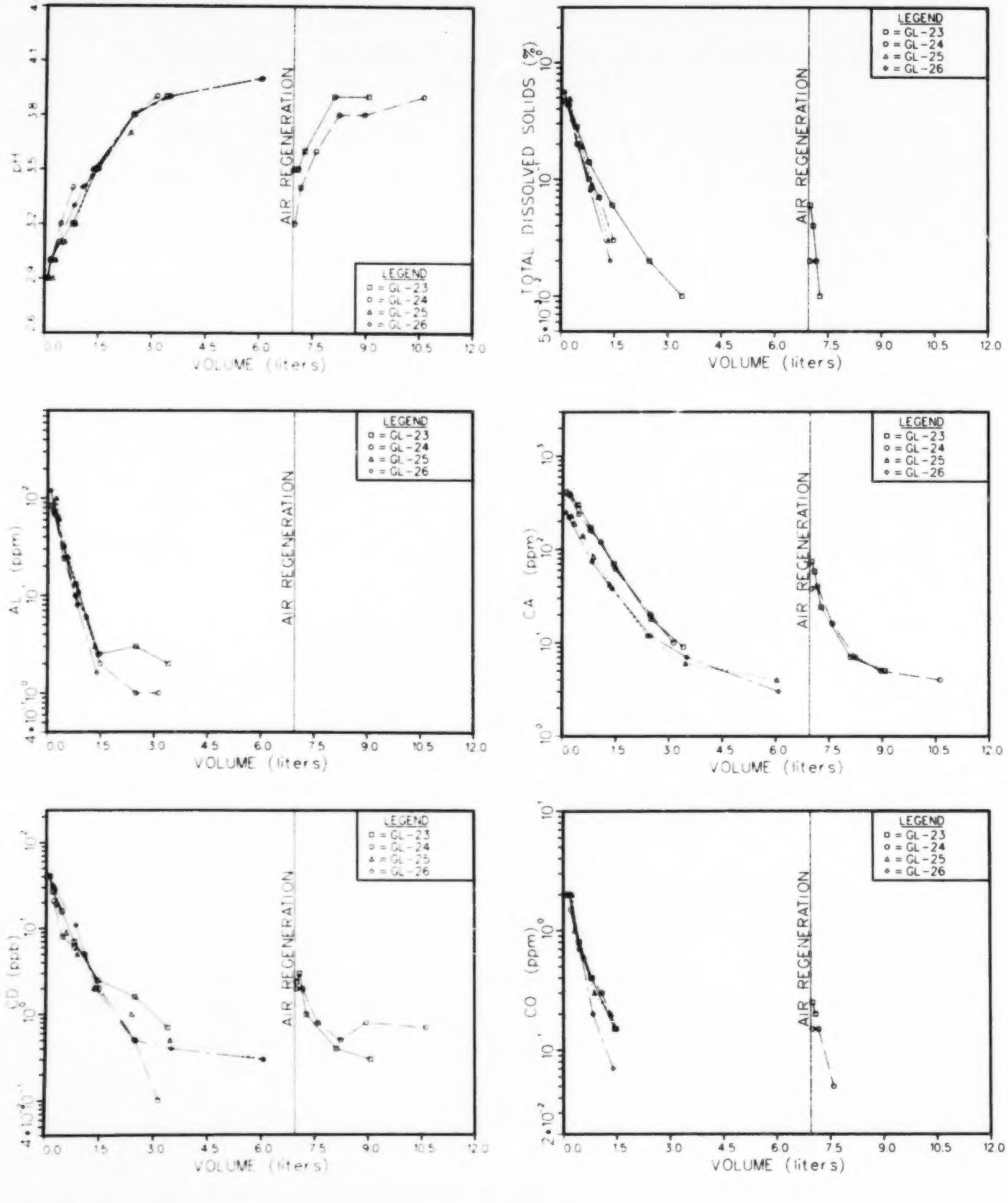


Fig. J-1.

Total dissolved solids, pH, and trace element levels for column leachings of Plant G, coal preparation waste.

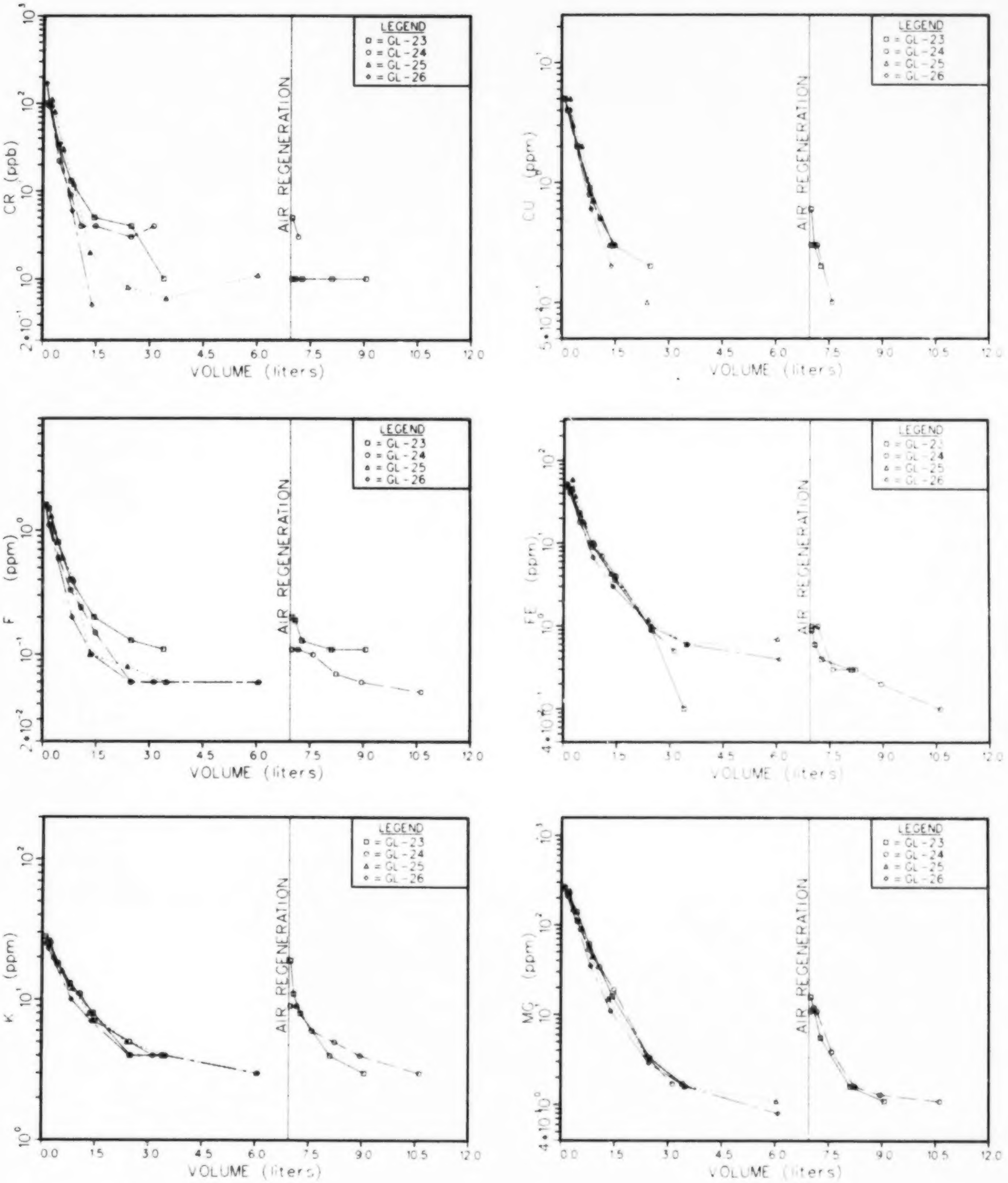


Fig. J-1 (contd).
Total dissolved solids, pH, and trace element levels for column leachings of Plant G, coal preparation waste.

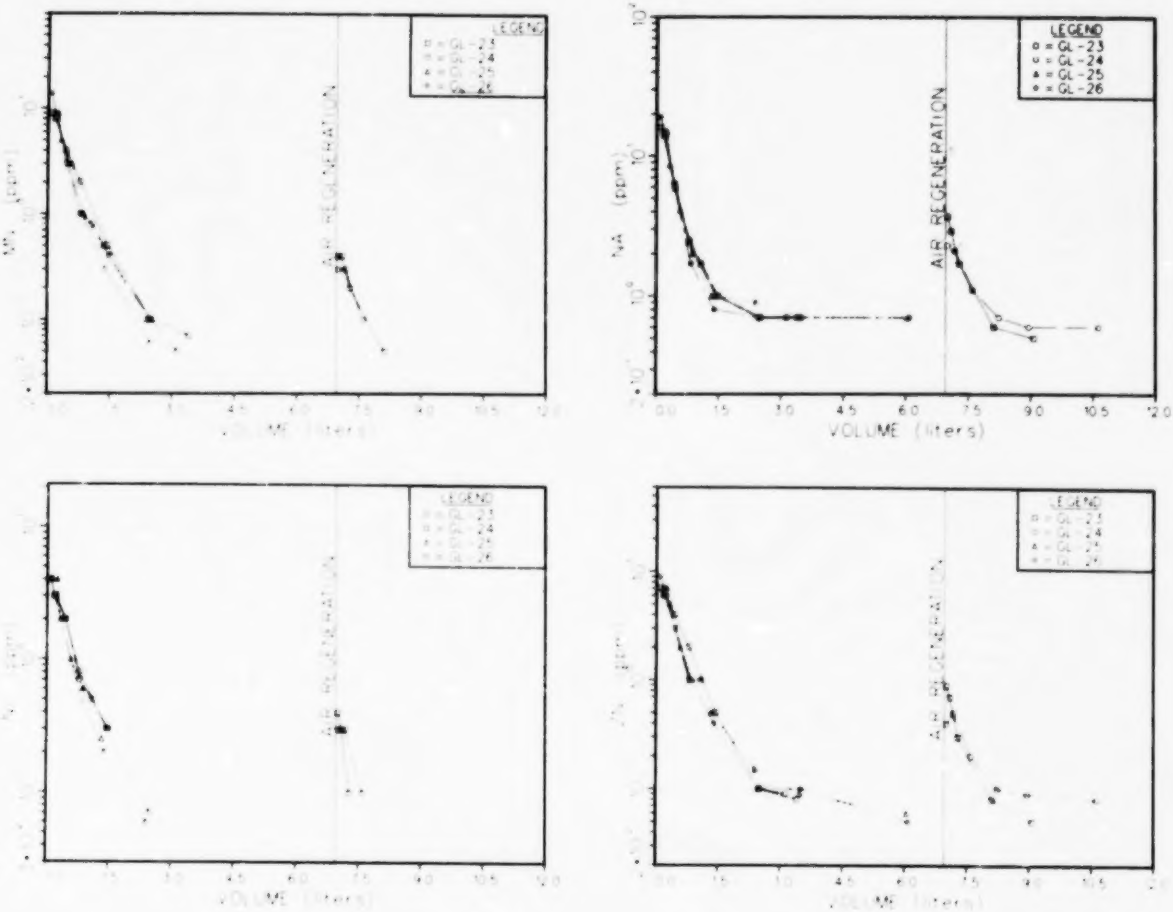


Fig. J-1 (contd).
Total dissolved solids, pH, and trace element levels for column leachings of Plant G, coal preparation waste.

TABLE J-V

DISCHARGE SEVERITY OF COLUMN LEACHATES FROM LOW-SULFUR AND HIGH-SULFUR COAL WASTES[a,f]

	Plant			
Element	**G[b]**	**A[c]**	**C[d]**	**B[e]**
Fe	4	80	90	500
Ni	3	10	20	50
Mn	0.8	3	2	4
Al	0.8	0.8	0.4	10
Cu	0.8	0.2	0.2	2
Zn	0.6	0.8	0.8	6
Ca	0.4	0.4	0.3	0.4
Cd	0.3	0.5	1	3
Co	0.08	0.3	0.5	1
K	0.01	0.02	0.04	0.01
Cr	0.004	0.001	0.03	0.02

---

[a] Based on element values at 2:5 leachate:waste ratio
Discharge Severity = leachate concentration/100/MATE value.

[b] Average of GL-23-2, GL-24-1, GL-25-1 and GL-26-2 data used.

[c] GL-19-2 data used.

[d] Average of GL-8-2 and GL-8-3 used.

[e] Average of GL-20-1 and GL-20-3 used.

[f] Health MATE used.

APPENDIX K
BIOASSAY RESULTS

LEVEL I BIOASSAY RESULTS FOR A COAL WASTE AND ITS LEACHATE[a,b]

Section	Test	EPA #	Performed by
1	Freshwater Algae	3.4.1	LASL
2	Fathead Minnows	3.4.2	LFE EAL, Richmond, CA
3	*Daphnia magna*	3.4.2	LFE EAL, Richmond, CA
4	Mutagenesis (AMES)	3.3.1	LASL
5	Rabbit Alveolar Macrophage (RAM)	3.3.2.1	LASL
6	Human Lung Fibroblast (WI-38)	3.3.2.2	LASL
7	Clonal Toxicity (CHO)	3.3.2.3	LASL
8	Quantal Rodent Toxicity	3.3.3	LASL

[a] Composition of CTWT-1012, called LEACHATE, under Freshwater Algae section.

[b] Solid waste used, called GOB, was Plant C, average, waste #18A; GL-21-1 is its 1 day leachate at 5 mℓ water/g waste.

I. FRESHWATER ALGAE

(V. Kollman, LASL)

Algal growth assays were based upon the principle of limiting nutrient supply to the growing organism. Growth of a specific alga was limited by the required nutrient which was present in shortest supply. The ecological effect studies using coal waste leachate were designed to determine biological responses to changes in macro- and micro-nutrients supplied by the waste material. Growth response was determined by adding a selected alga or various types of algae to the test water and measuring their growth at scheduled intervals. The test water was evaluated in its discharged concentration and in numerous dilutions combined with the appropriate minimal growth medium. Dilutions were used when the concentrated test solution was found to be toxic or greatly inhibitory to the test algae.

Seven types of algae -- three green species and four blue-green species -- and two types of diatoms were used as test organisms in these preliminary studies. *S. capricornutum*, *C. vulgaris*, *C. pyrenoidosa*, and the diatoms *Cyclotella sp.* and *P. tricornutum* were grown using cool white fluorescent lamps with an illumination intensity of 400 ft-candles. *M. aeruginosa*, *A. flos-aquae*, *A. nidulans*, and *S. maxima* were grown using 200 ft-candles. The temperature was maintained at 25°C and the cells were kept in suspension by oscillation of the cultures at 110 cpm.

The test organisms were transferred from agar slants to 30 mℓ of sterile, minimal Ecological Nutrient Medium (ENM) and grown for 7 days in a nutrient-stressed condition. Only 7-day cultures were used for inoculation of coal waste leachate samples, since these cultures were already in a stressed condition following their long-term exposure to a growth on minimal medium.

Nutrient-stressed organisms were cultured on various concentrations of coal-waste leachate. The diluted culture solutions were made by adding Ecological Nutrient Medium to the aqueous contaminant (see Table K-I). One set of test organisms was cultured on a medium in which the waste leachate was added at levels down to 0.75% of the medium. No

TABLE K-I

TRACE ELEMENT LEVELS IN LEACHATE USED FOR ALGAL TEST

	Leachate concentration		Diluted Leachate
Element	**Original**	**Diluted**	**+ Algal Medium**
F	110	1.65	-
Na	610	9.2	40
Al	553	8.30	24.1
K	17	0.26	0.68
Ca	540	8.10	22.7
Cr	0.52	0.01	0.04
Mn	16	0.24	0.79
Fe	5460	81.9	226
Co	5.9	0.09	0.28
Ni	12	0.18	0.52
Cu	1.6	0.02	0.06
Zn	24	0.36	1.12
Cd	0.31	0.005	0.017
pH	1.87		
TDS (%)	2.56		

---

*Values in μg/mℓ unless otherwise noted.

subsequent adjustment was made in the acidity (pH was 3 or less). All of these organisms died within 12 h after inoculation. Therefore, the EC_{50} was < 0.75%. A second set of test organisms was grown on coal leachate/ENM with the pH adjusted to 7.5. At concentrations up to 3% coal waste leachate and 97% ENM (pH 7.5), both green algae and blue-green algae grew at rates similar to those for the controls which were maintained on ENM only. Diatoms were not successfully cultured on either the ENM control or ENM plus coal-waste leachate. At concentrations of coal-waste leachate greater than 3%, the blue-green algae did not retain their viability; however, at concentrations up to and including 100% coal-waste leachate, the green alga *Chlorella pyrenoidosa* did retain a certain viability. Only at 50% or greater amounts of coal leachate was there significant loss of viability. At 50% coal-waste leachate and 50% ENM, 38% of the cells died. At 100% coal-waste leachate, 62% of the cells died. At concentrations of coal-waste leachate which were 10% or greater, there was no visible growth or increase in number of cells of *C. pyrenoidosa*. This may be due, in part, to the decrease in light transmission at the higher concentrations of coal-waste leachate. The order of adaptability and viability of the algae to the contaminant was green algae > blue-green algae > diatoms.

At concentrations of coal waste leachate between 0.75% and 3%, the algae grew at nearly normal rates. Under these conditions it can be expected that the growing organisms biologically metabolized or physically fixed some of the inorganic chemicals present in the contaminant.

The tests chosen to evaluate whether the coal waste materials could degrade the ecological systems were those under section 3.4 of EPA-600/7-77-043. The specific tests were 3.4.1 (freshwater algae) and 3.4.2 (both fathead minnows and *Daphnia magna*. The minnow and *Daphnia* tests were run by the Environmental Analysis Laboratories of LFE, Richmond, CA. The results are reported in Tables K-II and K-III. Only leachate was tested.

The tests chosen to evaluate the damage the coal waste leachates could cause to higher animals and humans were listed in the document EPA-600/7-77-043 [K. M. Duke, M. E. Davis, and A. J. Dennis, "IERL-RTP Procedures Manual: Level I Environmental Assessment, Biological Test for Pilot Plants" (April 1977)]. The specific sections used were 3.3.1 (Mutagenesis or AMES test), 3.3.2.1 (Rabbit Alveolar Macrophage or RAM), 3.3.2.2 (Human Lung Fibroblast or WI-38), 3.3.2.3 (Clonal Toxicity or CHO), and 3.3.3 (Quantal Rodent Toxicity). Each of these tests was run at LASL by personnel in our Life Sciences Division (LS-Division). Their results and observations are included in Tables K-IV through K-VII.

TABLE K-II
RESULTS FOR SENSITIVITY OF FATHEAD MINNOWS TO COAL WASTE LEACHATE

LFE ENVIRONMENTAL ANALYSIS LABORATORIES
2030 Wright Avenue
Richmond, CA 94804

STATIC BIOASSAY REPORT

Company: Los Alamos Scientific Lab.   Sample Identification: CTWT - 1012   LFE No.: 979-1-1

Date & Time Sampled: Date Received: 2/27/79   Date Started: 3/6/79   96 hr. TLM$_{96}$ 4,500 ppm

Control 1	6.3	9.8	16.2		10.2	17	10		9.8	17	10		10.0	16.0	10	6.8	9.8	17.9	10
Control 2	6.3	9.8	16.2		10.4	17	10		10.0	16	10		10.0	15.4	10	6.7	9.8	16.9	10
Percent Sample	Initial			24 hours				48 hours				72 hours				96 hours			
	pH	D.O.	Temp.	pH	D.O.	Temp.	Surv.	pH	D.O.	Temp.	Surv.	pH	D.O.	Temp.	Surv.	pH	D.O.	Temp.	Surv.
7,500 ppm	5.5	9.9	16.2		10.2	17	0		---	---	---		---	---	---	---	---	---	---
4,500 ppm	5.4	9.8	16.2		9.8	17	6		10.0	17.0	6		9.7	17.0	6	5.7	9.5	17.8	5
3,500 ppm	5.5	9.9	16.2		9.8	17	8		10.2	17.0	8		9.6	16.2	8	6.0	9.4	17.8	8
2,500 ppm	5.6	9.9	16.2		9.8	17	9		10.0	17.0	7		9.6	16.0	7	6.7	9.6	17.7	7
1,500 ppm	5.9	9.9	16.2		9.8	17	10		10.1	17.0	10		9.8	16.0	8	7.0	9.4	17.7	8
1,000 ppm	6.0	9.8	16.2		9.7	17	10		10.0	16.5	8		9.8	16.0	8	7.0	9.7	17.6	8

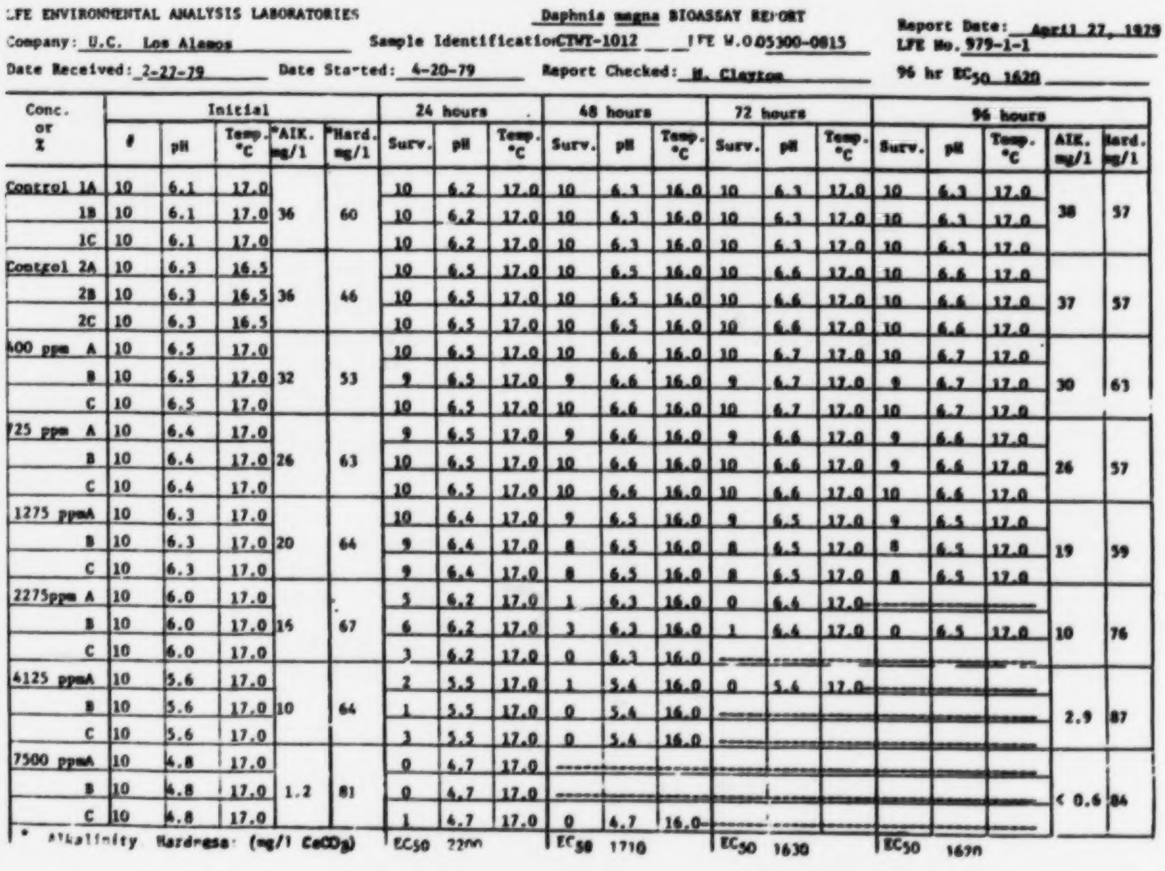
TLM$_{24}$ 4,900 ppm   TLM$_{48}$ 4,900 ppm   TLM$_{72}$ 4,900 ppm   TLM$_{96}$ 4.500 pp

Species: Fathead Minnow
Min. Length: 3.7 cm
Max. Length: 5.0 cm
Ave. Length: 4.5 cm
Min. Weight: 0.6 gm
Max. Weight: 1.9 gm
Ave. Weight: 1.2 gm

Vol. Test Soln.: 10 liters
Tank Depth: 28 cm
Type aeration: filtered air
No. of fish/conc.: 10 ea.
Acclimatization: 7 days @ 18°C
Mortality in Accl. tank: <1 %
Holding tank salinity: 0 ppt @ 20°C

TABLE K-III

RESULTS FOR SENSITIVITY OF *Daphnia magna* TO COAL WASTE LEACHATE



LFE ENVIRONMENTAL ANALYSIS LABORATORIES — *Daphnia magna* BIOASSAY REPORT — Report Date: April 27, 1979

Company: U.C. Los Alamos — Sample Identification: CTWT-1012 — LFE W.O. 05300-0815 — LFE No. 979-1-1

Date Received: 2-27-79 — Date Started: 4-20-79 — Report Checked: M. Clayton — 96 hr EC_{50} 1620

Conc. or %	Initial					24 hours			48 hours			72 hours			96 hours				
	#	pH	Temp. °C	*Alk. mg/1	*Hard. mg/1	Surv.	pH	Temp. °C	Surv.	pH	Temp. °C	Surv.	pH	Temp. °C	Surv.	pH	Temp. °C	Alk. mg/1	Hard. mg/1
Control 1A	10	6.1	17.0	36	60	10	6.2	17.0	10	6.3	16.0	10	6.3	17.0	10	6.3	17.0	38	57
1B	10	6.1	17.0			10	6.2	17.0	10	6.3	16.0	10	6.3	17.0	10	6.3	17.0		
1C	10	6.1	17.0			10	6.2	17.0	10	6.3	16.0	10	6.3	17.0	10	6.3	17.0		
Control 2A	10	6.3	16.5	36	46	10	6.5	17.0	10	6.5	16.0	10	6.6	17.0	10	6.6	17.0	37	57
2B	10	6.3	16.5			10	6.5	17.0	10	6.5	16.0	10	6.6	17.0	10	6.6	17.0		
2C	10	6.3	16.5			10	6.5	17.0	10	6.5	16.0	10	6.6	17.0	10	6.6	17.0		
400 ppm A	10	6.5	17.0	32	53	10	6.5	17.0	10	6.6	16.0	10	6.7	17.0	10	6.7	17.0	30	63
B	10	6.5	17.0			9	6.5	17.0	9	6.6	16.0	9	6.7	17.0	9	6.7	17.0		
C	10	6.5	17.0			10	6.5	17.0	10	6.6	16.0	10	6.7	17.0	10	6.7	17.0		
725 ppm A	10	6.4	17.0	26	63	9	6.5	17.0	9	6.6	16.0	9	6.6	17.0	9	6.6	17.0	26	57
B	10	6.4	17.0			10	6.5	17.0	10	6.6	16.0	10	6.6	17.0	9	6.6	17.0		
C	10	6.4	17.0			10	6.5	17.0	10	6.6	16.0	10	6.6	17.0	10	6.6	17.0		
1275 ppmA	10	6.3	17.0	20	64	10	6.4	17.0	9	6.5	16.0	9	6.5	17.0	9	6.5	17.0	19	59
B	10	6.3	17.0			9	6.4	17.0	8	6.5	16.0	8	6.5	17.0	8	6.5	17.0		
C	10	6.3	17.0			9	6.4	17.0	8	6.5	16.0	8	6.5	17.0	8	6.5	17.0		
2275ppm A	10	6.0	17.0	15	67	5	6.2	17.0	1	6.3	16.0	0	6.6	17.0	—	—	—	10	76
B	10	6.0	17.0			6	6.2	17.0	3	6.3	16.0	1	6.6	17.0	0	6.5	17.0		
C	10	6.0	17.0			3	6.2	17.0	0	6.3	16.0	—	—	—	—	—	—		
4125 ppmA	10	5.6	17.0	10	64	2	5.5	17.0	1	5.4	16.0	0	5.6	17.0	—	—	—	2.9	87
B	10	5.6	17.0			1	5.5	17.0	0	5.4	16.0	—	—	—	—	—	—		
C	10	5.6	17.0			3	5.5	17.0	0	5.4	16.0	—	—	—	—	—	—		
7500 ppmA	10	4.8	17.0	1.2	81	0	4.7	17.0	—	—	—	—	—	—	—	—	—	< 0.6	84
B	10	4.8	17.0			0	4.7	17.0	—	—	—	—	—	—	—	—	—		
C	10	4.8	17.0			1	4.7	17.0	0	4.7	16.0	—	—	—	—	—	—		
* Alkalinity Hardness: (mg/1 $CaCO_3$)						EC_{50}	2200		EC_{50}	1710		EC_{50}	1630		EC_{50}	1620			

II. MUTAGENESIS (AMES)

(B. Barnhart and S. Wang, LASL)

Negative responses were obtained with and without S-9 activation for both coal-waste leachate (LEACHATE) and solid coal waste (GOB). The number of spontaneous revertants/plate was within acceptable limits for the test strains used.

Strain	Spontaneous Revertants/plate
TA-98	>50 ± 25
TA-100	>150 ± 75
TA-1535	>20 ± 10
TA-1537	>15 ± 10

III. RABBIT ALVEOLAR MACROPHAGE (RAM)

(L. M. Holland and J. Wilson, LASL)

TABLE K-IV

RESULTS OF RABBIT ALVEOLAR MACROPHAGE (RAM) TEST ON A COAL WASTE AND ITS LEACHATE

Dose[a] (mℓ/mℓ)	Viability (%)
0	92
0.006	77,75
0.02	74,57
0.06	71,40
0.2	3
0.6	Too few cells
0.075(Est)	50

---

[a] pH adjusted to 7.3-7.6;
precipitate formed;
CTWT-1012 used.

IV. HUMAN LUNG FIBROBLAST (WI-38)

(A. Stroud, LASL)

TABLE K-V

RESULTS OF HUMAN LUNG FIBROBLAST (WI-38) TEST ON A COAL WASTE AND ITS LEACHATE

Leachate		Gob	
Dose (mℓ/mℓ)[a]	Surviving (%)	Dose (mg/mℓ)[a]	Surviving (%)
0	100	0	100
0.01	94.5	0.05	83.2
0.02	84.8	0.10	80.9
0.03	82.5	0.50	77.2
0.04	76.7	1.0	60.8
0.11(Est)	50	1.84(Est)	50

---

[a] Dose applied 20 hours after incubation; 40 hour total test period. 5 mℓ total size; CTWT-1012 used.

Observations

Leachate test samples were significantly different from controls, except at the low (0.01 mℓ/mℓ) dose.

Gob (waste) test samples were similar to one another but were different from the control. Cells were more sensitive to the gob than they were to the leachate.

V. CLONAL TOXICITY (CHO)

(A. Stroud, LASL)

TABLE K-VI

RESULTS OF CLONAL TOXICITY (CHO) TEST FOR COAL WASTE LEACHATE

	Surviving Fraction (%)			
	20-hour Inoculation[b]		1-week Inoculation[b]	
Dose[a] (mℓ/mℓ)	24 Hour[c]	48 Hour[c]	24 Hour[c]	48 Hour[c]
0	100	100	100	100
0.0025	-	-	94.7	99.4
0.0125	79.6	65.3	85.5	90.7
0.025	65.4	57.9	85.8	88.6
0.05	0.02	0.02	-	-

---

[a] Total media was 4 mℓ; CTWT-1012 used.

[b] Time after incubation before inoculation.

[c] Duration of treatment.

Observation

Colonies became detached and were floating around in the media in the higher dose samples.

TABLE K-VII

RESULTS OF CLONAL TOXICITY (CHO) TEST FOR COAL WASTE SOLID

	Surviving Fraction (%)			
Dose[a] (mg/mℓ)	20-hour Inoculation[b] 24 Hour[c]	20-hour Inoculation[b] 48 Hour[c]	1-week Inoculation[b] 24 Hour[c]	1-week Inoculation[b] 48 Hour[c]
0	100	100	100	100
0.05	79.6	72.6	91	90.7
0.10	68.3	60.2	91.2	92.4
0.50	15.0	11.1	87.3	86.7
1.0	3.5	1.7	81.6	83.5
5.0	2.2	1.3	-	-

---

[a] Total media was 5 mℓ; gob (#18A) prepared as suspension in 0.85% NaCl solution.
[b] Time after incubation before inoculation.
[c] Duration of treatment.

VI. QUANTAL RODENT TOXICITY

(J. Wilson, LASL)

Tests using the quantal method established the acute, in vivo, toxicity of a coal-waste leachate (LEACHATE) and coal waste (GOB) as having an LD_{50} greater than 10 g/kg. This test used male and female rats given one acute intragastric dose of 10 g or 10 mℓ per kg body weight followed by 2 weeks of observation. There were no gross lesions at sacrifice.

APPENDIX L

pH-CONTROLLED LEACHING OF COAL WASTE, FLY ASH, AND SOIL

The following procedures were followed: 50-g portions of Plant B waste (24A, ground to -20 mesh) were placed in 500-mℓ Erlenmeyer flasks equipped with ground glass stoppers. The leaching solutions were prepared according to the descriptions given in Table L-I. Each 200 mℓ of leaching solution was added to the flasks and the pH adjusted with 0.1N sodium hydroxide. The flasks were purged with argon, capped, sealed with Parafilm, and placed on a reciprocating shaker. The flask contents were mixed with ninety 3-1/2-in. strokes per min for 48 h with one interruption at the 24-h point to adjust the pH and repurge. At the end of the leach period, the contents of the flasks were vacuum filtered under argon through Whatman #42 paper and refiltered through 0.45 μm Millipore filters. The filtrate was analyzed for pH and trace element concentrations. The results are posted in Tables L-II to L-IV. Plots are presented in Figs. 30 and 31 of the text and Fig. L-1.

TABLE L-I

LEACHING SOLUTION COMPOSITIONS FOR pH-CONTROLLED LEACHING[a]

CTWT-18	Buffer Soln[b]	1N NaOH (mℓ)[c]	Additive
1	20 mℓ of A	-	-
2	-	-	-
3	20 mℓ of B	20 (+ 3[c])	-
4	200 mℓ of C	15 (+ 4[c])	-
5	20 mℓ of D	20 (+ 60[c])	12.4g $NH_2OH \cdot HCl$
6	20 mℓ of D	20 (+ 3[c])	-
7	20 mℓ of D	33 (+ 1[c])	20 mℓ of 30% H_2O_2
8	20 mℓ of E	20 (+ 10[c])	-

---

[a] Deionized water to give 200 mℓ.

[b] Buffer A: 0.5M H_2SO_4 and 0.5M Na_2SO_4
B: 0.5M H_3PO_4 and 0.5M NaH_2PO_4
C: 4.9g HOAc + 3.7g NaOAc in 1 liter water (ASTM method B)
D: 0.5M NaH_2PO_4 and 0.5M Na_2HPO_4
E: 0.5M $NaHCO_3$ and 0.5M Na_2CO_3

[c] This NaOH was added as the leaching progressed to control pH.

TABLE L-II

EFFECT OF ACIDITY ON THE LEACHING OF EASTERN FLY ASH[a]

#	Buffer	Comment	pH	Ca	Fe
1a	H_3PO_4[b]		2.04	510	400
b	"		2.06	580	380
2a	H_2SO_4		2.82	430	120
b	"		3.14	425	120
3a	H_3PO_4		3.81	450	0.20
b	"		3.91	410	0.06
4a	HOAc		4.55	320	1.38
b	"		4.56	320	1.49
5a	HOAc	TEP[c]	5.00	52	0.03
b	"		5.00	49	0.03
6a	-	Control	5.20	260	0.02
b	-		5.43	310	0.01
7a	-	H_2O_2[d]	5.47	235	0.01
b	-	"	5.56	230	0.01
8a	NaH_2PO_4		6.76	14.8	0.01
b	"		6.76	14.8	0.01
9a	Na_2HPO_4		9.72	7.2	0.32
b	"		9.73	7.2	0.32

[a] From ASTM, Phase I, leaching round robin; run in duplicate.

[b] Extra acid to lower pH.

[c] Original, EPA, TEP leaching test.

[d] Added to oxidize ferrous to ferric.

TABLE L-III

EFFECT OF ACIDITY ON THE LEACHING OF AN ILLINOIS SOIL[a]

#	Buffer	Comment	pH	Ca	Fe
1a	H_2SO_4		1.77	280	220
b	"		1.88	290	220
2a	H_3PO_4		2.00	220	360
b	"		2.06	190	310
3a	-	H_2O_2[b]	3.85	4.3	0.62
b	-	"	5.40	4.2	0.50
4a	HOAc		4.54	58	0.01
b	"		4.55	68	0.02
5a	HOAc	TEP[c]	5.00	0.69	0.10
b	"	"	5.00	0.92	2.10
6a	-	Control	5.62	2.93	0.06
b	-	"	5.72	1.52	1.42
7a	NaH_2PO_4		6.62	16.0	0.33
b	"		6.64	16.4	0.16
8a	Na_2HPO_4	9.51	6.8	0.20	
b	"		9.57	6.6	0.60

[a] From ASTM, Phase I, leaching round robin; run in duplicate.

[b] Added to oxidize ferrous to ferric (note Ca reduction, too).

[c] Original, EPA, TEP leaching test.

TABLE L-IV

EFFECT OF ACIDITY ON THE LEACHING OF AN ILLINOIS BASIN COAL WASTE[a]

CTWT−18	BUFFER	COMMENT	pH[b]	Al	As	Ca	Cd	Co	Cr	Cu	F	Fe[c]	Mn	Mo	Ni	Zn
1	H_2SO_4		1.39	240	1.7	170	.02	3.7	.19	.2	4.6	2740	6.7	.1	6.1	10
2	–	Control	1.91	220	.9	150	.02	3.6	.16	.02	5.7	2430[d]	6.7	.1	5.9	10
3	H_3PO_4		2.94	29	1.2	120	.02	3.3	.09	.01	.8	1360	5.7	<.1	5.9	6
4	HOAc		4.45	32	.09	120	.02	3.1	.01	.02	1.7	1480	6.0	<.1	5.6	7
5	NaH_2PO_4	NH_4OH	4.51	.6	.69	90	.012	.6	<.01	.02	.7	8	1.2	<.1	2.4	.2
6	NaH_2PO_4		5.95	<.2	.7	12	.003	<.01	<.01	<.01	.6	17	.09	.4	.06	.04
7	NaH_2PO_4	H_2O_2	6.24	<.2	.28	13	<.003	.1	<.01	<.01	.3	3	.1	.6	.6	.03
8	Na_2HPO_4		8.98	<.2	.01	7	<.003	<.01	<.01	<.01	2.2	.4	<.02	1.2	<.02	.01

---

[a] 50 g waste (Plant B, -20 mesh) leached with 200-260 mℓ of solution; argon atmosphere used. Data normalized to 250 mℓ.

[b] Final pH value before filtering.

[c] Approximately all Fe^{+2}.

[d] 2400 ppm Fe^{+2} and 30 ppm Fe^{+3}.

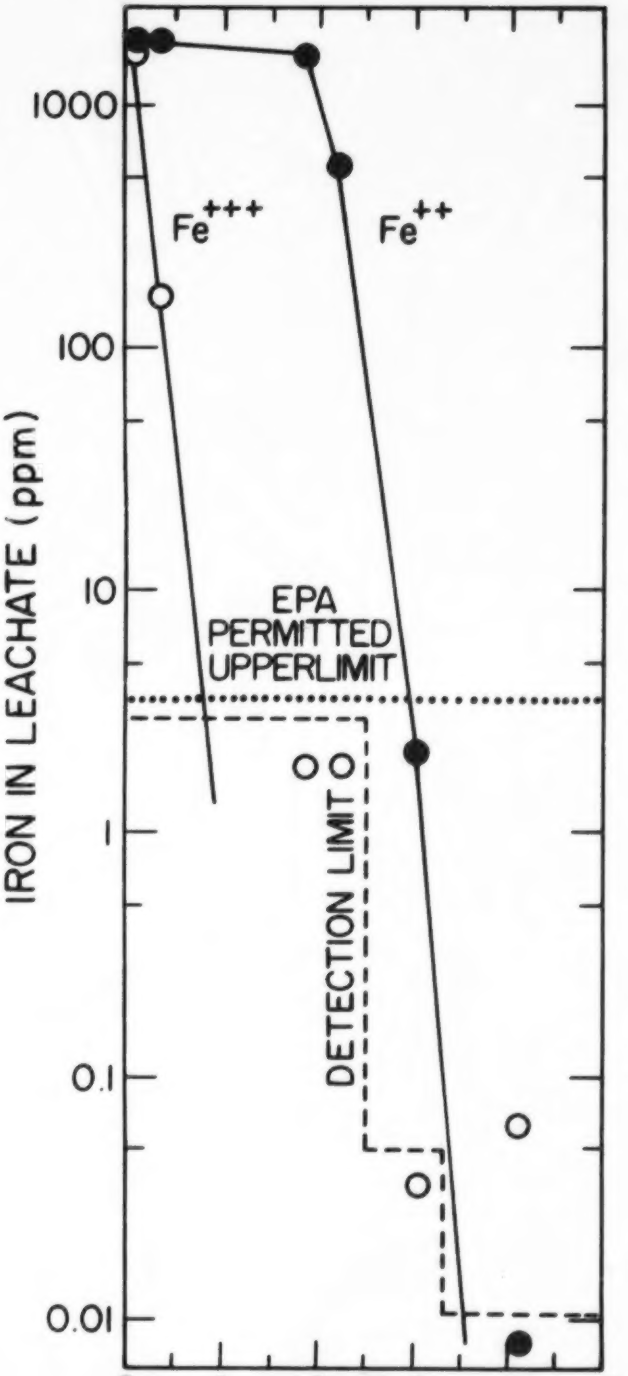


Fig. L-1.
The pH influence on the leachability of iron from an Illinois Basin coal waste.

APPENDIX M

ATTENUATION OF SEVERAL TRACE ELEMENTS IN A COAL-WASTE LEACHATE PASSED THROUGH COLUMNS OF SOILS

Two Illinois soils were selected for a preliminary column attenuation study. The soils selected were a noncalcareous, weathered loess (No. 20 in Table XIV of the third annual report) and an unweathered, calcareous till (No. 110 in Table XIC of the third annual report). The leachate was CTWT-1012, which is a highly contaminated coal refuse leachate. The experiment was performed under an argon atmosphere to prevent air oxidation of iron from ferrous to ferric. Approximately 55 g of each soil (less than 100 mesh) was placed in a glass column, and leachate was passed downward through the column under a head of about 3 - 4 in. Flow was around 1 mℓ/h. The pH, Fe++ and total Fe were monitored for column influent and effluent. Ferric iron was calculated as the difference between total and ferrous iron and has a very large error. Selected effluent aliquots were further analyzed for the elements Al, Ca, Mn and Ni. Results of this experiment are tabulated in Tables M-I and M-II. Plots can be found in Figs. 37 and 38 of the text.

TABLE M-I

ATTENUATION OF TRACE ELEMENTS IN A COAL WASTE LEACHATE BY A COLUMN OF UNWEATHERED, CALCAREOUS SOIL[a]

Sample	Effluent Volume(ml)	pH	Al	Ca	Mn	Fe^{+2}	Fe^{+3}	Fe^{TOTAL}	Ni
Original Leachate	0 σ	2.0	560 ±20	500 ±50	14.2 ±0.5	4000 ±300	700 ±200	4700 ±200	12.6 ±0.3
1	28	6.2	4.1	550	23.2	1800	100	1900	6.5
3	106	5.5	27.2	500	22.8	4100	100	4200	11.9
4	160	6.0	5.1	400	23.0	4200	0	4200	11.7
5	195	–	1.0	450	25.2	–	–	4400	13.1
6	226	5.7	5.9	450	22.6	4300	0	4300	11.8
7	255	6.1	4.8	450	22.2	4000	0	4000	11.9
8	285	6.0	7.2	550	26.3	4600	0	4600	13.2
9	310	4.4	8.0	550	23.5	3600	100	3700	11.9
10	320	3.7							

[a] Soil properties: pH-8.2; CO_3 - 13.4%; clay - 16.1%; CEC - 7.7 meq/100g; organic matter - 0.91%.

TABLE M-II

ATTENUATION OF TRACE ELEMENTS IN A COAL WASTE LEACHATE BY A COLUMN OF WEATHERED AND LEACHED SOIL[a]

Sample	Effluent Volume (ml)	pH	Al	Ca	Mn	Fe^{+2}	Fe^{+3}	Fe^{TOTAL}	Ni
Original	0	2.0	560	520	14.2	4000	700	4700	12.6
Leachate	σ		±20	±50	±0.5	±300	±200	±200	±0.3
1	17.5	–	430	500	120	1800	300	2100	8.0
2	54	3.9	570	720	215	1900	300	2200	11.6
3	93	3.5	920	510	62	3800	200	4000	13.0
4	134	3.1	1170	640	38	5000	500	5500	18.3
5	191	2.4	750	530	19	5200	500	5700	14.0
6	251	2.2	730	530	18.0	5100	100	5200	13.8
7	272	2.1	710	540	18.3	4200	700	4900	14.3
8	343	2.1	640	510	16.5	4900	400	5300	13.3
9	387	2.2	640	510	16.6	3700	500	4200	12.8
10	430	2.2	690	560	18.9	4700	200	4900	15.1
11	476	2.0	690	580	17.6	4600	600	5200	14.6

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[a] Soil properties: pH - 5.6; $CO_3^{=}$ - 0.0%;
clay - 35.9%; CEC - 27.9 meq/100g; organic matter - 0.47%.

APPENDIX N

SPARK SOURCE MASS SPECTROMETRY SAMPLE PREPARATION AND ANALYSIS

(R. M. Abernathy, C. F. Hammond, J. E. Alarid,
S. F. Marsh, and J. E. Rein), LASL

Multielemental, quantitative analysis of coal materials by spark source mass spectrometry (SSMS) requires chemical pretreatment of the sample to destroy remaining organic components, which produce charged ions over the entire atomic mass region. A two-step dissolution treatment has been developed that completely eliminates organic components and ensures a homogeneous distribution of sample elements and the added internal standard(s). The dissolution consists of igniting pulverized samples in air at 500°C for 4 h and dissolving the ash completely in an acid mixture using a LASL-developed, Teflon-container, metal-shell apparatus (now manufactured by the Parr Instrument Company). The acid mixture is 6 volumes 12M HCl, 1 volume 15.6M HNO_3, 1 volume 29M HF, and 2 volumes water. Dissolution of 100 mg of coal ash in 5 mℓ acid mixture is accomplished in 12 hours at 200°C. The solution of the ash and a measured portion of the internal standard solution are added to 150 mg of graphite (spectroscopic grade) in a polyfluorinated plastic container. The mixture is dried and ground with a mortar. Ethanol is added and the mixture is again dried, homogenized in a Wig-L-Bug mixer, and pressed into an electrode.

For the initial analyses, an erbium internal standard and photoplate detection were used. A major effort is under way to establish more accurate sensitivity factors for about 70 elements and to develop a procedure in which different internal standard elements will be used at low, medium, and high mass regions. Current results for NBS 1632 coal are listed in Table N-I.

TABLE N-I

TRACE ELEMENT LEVELS IN NBS 1632 COAL BY SPARK SOURCE MASS SPECTROMETRY[a]

Element	Literature [b]	LASL [c]	Element	Literature[b]	LASL [c]
Ag	(<0.1) [d]	0.1	Mo	3.4 [h]	1
Al	18500 [f]	3900	Na	414 [f]	450
As	5.9 [d]		Nb	11 [g]	1
Au		<0.01	Nd	6 [g]	8
B	50 [g]	4	Ni	15 [d]	30
Ba	352 [f]	220	P	71 [i]	80
Be	(1.5) [d]		Pb	30 [d]	20
Bi	0.4 [g]	0.05	Pd		20
Br	8 [g]		Pr	2 [g]	2
Ca	4300 [f]	1600	Pt		<0.1
Cd	0.19 [d]	0.2	Rb	21 [f]	19
Ce	19.5 [f]	16	Rh		0.1
Cl	890 [f]	250	Ru		0.01
Co	5.9 [f]	(1600.) [j]	S	14300 [i]	30 [e]
Cr	20.2 [d]	15	Sb	3.9 [f]	
Cs	1.4 [f]	0.06	Sc	3.7 [f]	5
Cu	18 [d]	70	Se	2.9 [d]	2
Dy	2 [g]	1	Si	(32000.) [d]	
Er	0.7 [g]	0.9	Sm	1.7 [f]	2
Eu	0.33 [f]	0.7	Sn	2 [g]	4
F	500.[g]		Sr	161 [f]	95
Fe	8700 [d]	3500	Ta	0.24 [f]	
Ga	8.5 [h]	2	Tb	0.4 [g]	2
Gd	1 [g]	6	Te	(<0.1) [d]	0.3
Ge	1 [g]	0.7	Th	3.2 [f]	1
Hf	0.96 [f]	4	Ti	1100 [f]	2800
Hg	0.12[d]		Tl	0.59 [d]	0.3
Ho	1 [g]	0.4	Tm	0.2 [g]	0.5
I	2 [g]	0.2 [e]	U	1.4 [d]	0.4
Ir		0.3	V	35 [d]	20
K	2800 [f]	5600	W	<1 [g]	
La	10.7 [f]	9	Y	7 [g]	5
Li	60 [g]	30	Yb	<1 [g]	0.4
Lu	<0.3 [g]	0.4	Zn	37 [d]	15
Mg	2000 [f]	570	Zr	45 [h]	15
Mn	40 [d]	25			

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[a] Elemental concentrations are in ppm.

[b] "Best" of a number of sources.

[c] Others: AA and NAA data; SSMS: spark source mass spectroscopy.

[d] NBS values; those in parentheses are not certified.

[e] Volatile; some or extensive loss during dissolution expected.

[f] Ondov *et al. Analytical Chemistry* 47, 1102 (1975).

[g] Private communication from Commercial Testing and Engineering Co.

[h] Klein *et al. Environmental Science and Technology* 9, 973 (1975).

[i] LASL (LA-6835-PR, 1st Annual Report).

[j] Contaminated during sample preparation?

APPENDIX O

RAINWATER FLOW THROUGH A COAL WASTE DUMP

The bulk density of high-sulfur coal preparation waste is approximately 125 lb/ft^3. A 30-ft high pile of this waste would occupy an area 326 ft square or 100,000 ft^2. In a location receiving 30 in. of rain per year, 42 mℓ of water per kilogram of waste would enter the pile if 100% percolation is allowed. Laboratory column leaching shows that 2 ℓ of water are needed to wash the pollutants from each kilogram of the waste. Without the intrusion of groundwater, 48 years would be required to purge the pile if the waste did not generate further pollutants and if all the rain percolated through the waste. Rainwater runoff and evaporation and waste oxidation would increase the time, while groundwater recharge would reduce it.

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16. ABSTRACT

The report describes progress during the year of a trace element characterization of coal wastes. Assessments continued of low-sulfur coal wastes from the Appalachian Region, including mineralogical and trace element analyses of the materials, and studies of their weathering and leaching behavior. Although the acid-forming mineral (pyrite and marcasite) concentrations were very low, leachates were quite acid (pH < or = 3) with concomitant trace element (Al, Mn, Fe, Ni, Cu) concentration elevation. Bioassays, part of the overall assessment of the degree of environmental concern associated with acidic coal waste drainage, revealed that coal wastes and their leachates are toxic to freshwater algae, fathead minnows, and a species of freshwater flea. Experiments to identify control options for coal wastes and their drainage have focused on predisposal and co-disposal waste treatment, with technical and economic evaluations of the most promising options. One of the most promising is waste pretreatment with a lime/limestone mixture, producing a waste with no acid-forming tendencies for up to several months, during which time it may be possible to dispose of the treated waste in a nonreactive environment. The cost of this option compares to that of the commonly used lime neutralization of acid drainage.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Weathering	Pollution Control	13B	
Coal	Leaching	Stationary Sources	08G	07A
Waste Treatment	Bioassay	Coal Wastes		06A
Properties	Toxicity	Characterization	14G	06T
Analyzing	Calcium Oxides	Trace Elements	14B	07B
Chemical Analysis	Calcium Carbonates		07D	
	Sludge			

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